Supporting Information

Synthesis of 6-Aminophenanthridines via Palladium-Catalyzed Insertion of Isocyanides into *N*-Sulfonyl-2-aminobiaryls

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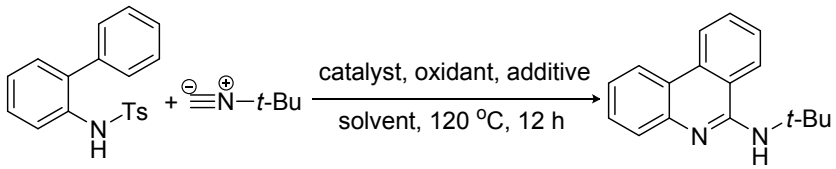
General Information

^{1}H and ^{13}C NMR spectra were recorded on BRUKER DRX/400 spectrometer using $CDCl_3$ as solvent and TMS as an internal standard. Gas chromatograph mass spectra were obtained with a SHIMADZU model GCMS/QP5000 spectrometer. IR spectra were obtained as potassium bromide pellets or as liquid films between two potassium bromide pellets with a Brucker Vector 22 spectrometer. TLC was performed using commercially prepared 100/400 mesh silica gel plates (GF254), and visualization was effected at 254 nm. All the other chemicals were purchased from Aldrich, Acros and Alfa Aesar Chemicals.

Optimization Study [a]

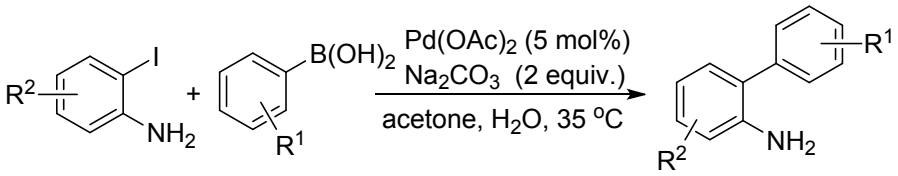


1a **2a** **3aa**

entry	catalyst	solvent	oxidant	Yield [b] (%)
1	$Pd(PPh_3)Cl_2$	DMSO	$Cu(OAc)_2$	10
2	$Pd(OAc)_2$	DMSO	$Cu(OAc)_2$	25
3	$PdCl_2$	DMSO	$Cu(OAc)_2$	<5
4	$Pd(OAc)_2$	DMSO	CuO	10
5	$Pd(OAc)_2$	DMSO	$Cu(OTf)_2$	<5
6	$Pd(OAc)_2$	DMSO	$CuCl_2$	n.d.
7	$Pd(OAc)_2$	DMSO	$Cu(TFA)_2 \cdot xH_2O$	10
8	$Pd(OAc)_2$	Toluene	$Cu(OAc)_2$	20
9	$Pd(OAc)_2$	Dioxane	$Cu(OAc)_2$	20
10	$Pd(OAc)_2$	MeCN	$Cu(OAc)_2$	trace
11	$Pd(OAc)_2$	DMF	$Cu(OAc)_2$	trace
12	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	78
13[c]	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	85
14[d]	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	5
15[e]	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	78
16[f]	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	90 (88)
17[g]	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	78
18[h]	$Pd(OAc)_2$	DCE	$Cu(OAc)_2$	75

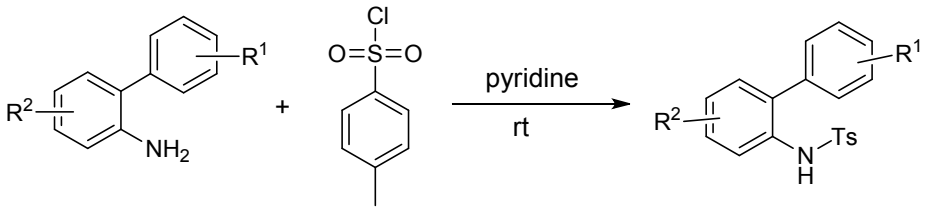
[a] Reaction conditions: All reactions were performed with **1a** (0.1 mmol), **2a** (0.15 mmol), catalyst (10 mol %), ligand (10 mol %) base (0.2 mmol), oxidant (0.2 mmol), and H_2O in solvent (2.0 mL) at 120 °C for 12 h unless otherwise noted . [b] Yeilds and conversions analyzed by GC/MS are based on **1a**, n.d. = not detected. [c] addition of H_2O (0.4 mmol), [d] addition of H_2O (0.4 mmol) and Cs_2CO_3 (0.2 mmol), [e] addition of H_2O (0.4 mmol) and Na_2CO_3 (0.2 mmol), [f] addition of H_2O (0.4 mmol) and $NaHCO_3$ (0.2 mmol), [g] Reaction time was 24 h. [h] Reaction temperature was 130 °C.

General Procedure for the Synthesis of Biphenylamine Derivatives[1]



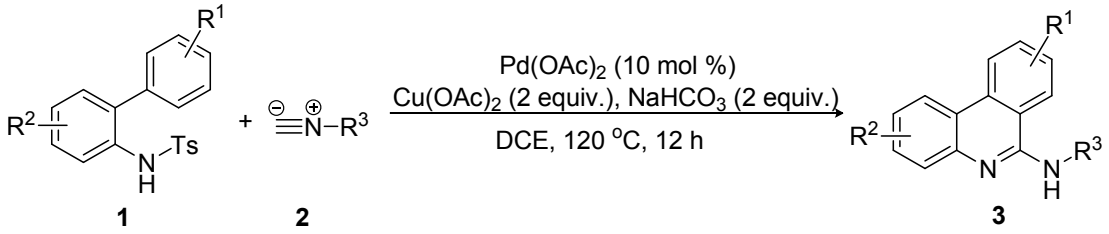
To an oven dried 50 mL round bottom flask equipped with a magnetic stir bar, was added 2-iodioanilines (5.0 mmol), arylboronic acids (7.5 mmol), Na_2CO_3 (10 mmol) and $Pd(OAc)_2$ (5 mol%), distilled water (15 mL) and acetone (15 mL). The reaction mixture was stirred at 35 °C overnight. Afterwards the mixture was filtered through a plug of Celite. The filtrate was extracted for several times with diethyl ether, and the combined organic layers were washed with brine and dried over $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was separated by column chromatography (hexanes/EtOAc) to give the target product.

General Procedure for Preparation of *N*-Sulfonyl-2-aminobiaryls[1]



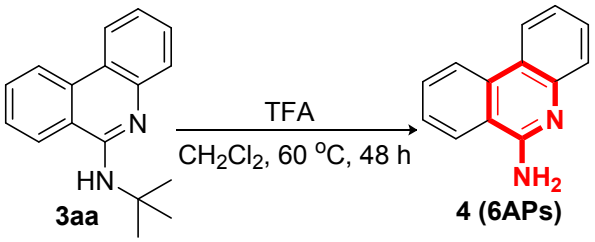
To an oven dried 50 mL round bottom flask containing the solution of 2-Aminobiaryls (5.0 mmol) in pyridine (10 mL), arylsulfonyl chlorides (7.5 mmol) was added. Then the mixture was stirred at room temperature for 12 h. Upon completion, the reaction mixture was washed with saturated NaCl for three times and extracted with ethyl acetate (3×10 mL), and the organic layers were combined, dried over anhydrous $MgSO_4$. The organic layer was then concentrated under vacuum, and the residue was separated by silica gelcolumn chromatography (hexanes/EtOAc) to give *N*-sulfonyl-2-aminobiaryls.

General Procedure for the Synthesis of 6-Aminophenanthridine Derivatives [1]



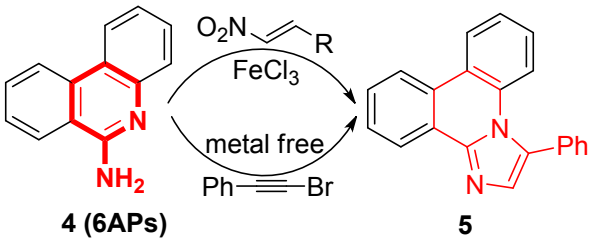
To a sealed tube *N*-sulfonyl-2-aminobiaryl (0.1mmol), $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2$ (0.2 mmol), $NaHCO_3$ (0.2 mmol), H_2O (0.4 mmol) and DCE (2 mL) were added and stirred for three minutes at room temperature, then isocyanide (1.5 mmol) was added and stirred at 120 °C for 12 h. After cooling to room temperature, the mixture was extracted by ethyl acetate (3×10 mL). The organic layer was washed with brine, and dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was isolated by silica gel column chromatography, eluted with petroleum ether/ethyl acetate to give the pure product **3**.

General Procedure for the Synthesis of 6-Aminophenanthridine[2]



A magnetically stirred solution of *N*-(*tert*-butyl)phenanthridin-6-amine (**3aa**) (1 mmol) in CH_2Cl_2 was treated with trifluoroacetic acid (2 mL) and the ensuing mixture heated at reflux for 48 h. The cooled reaction mixture was diluted with CH_2Cl_2 (5 mL) and the pH adjusted to 9–10 with Na_2CO_3 (saturated aqueous solution). The separated aqueous layer was extracted with ethyl acetate (5 × 100 mL) and the combined organic extracts were then dried (Na_2SO_4), filtered and concentrated under reduced pressure. The white solid thus obtained was subjected to flash chromatography (silica, 2:98→5:95 v/v MeOH/CH_2Cl_2 gradient elution) to afford, after concentration of the relevant fractions (R_f = 0.2 in 1:19 v/v MeOH/CH_2Cl_2), compound **4**, 73%) as a yellow solid.

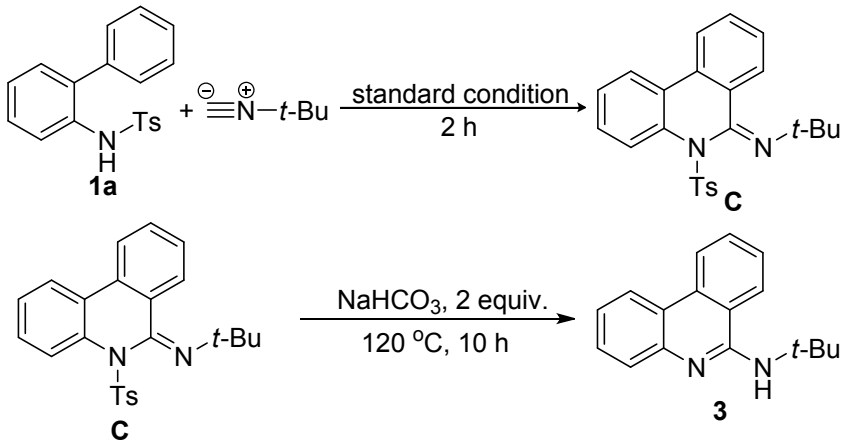
General Procedure for the Synthesis of 3-Phenylimidazo[1,2-f]phenanthridine (5)[3][4]



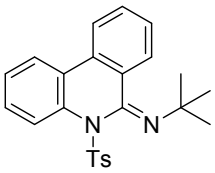
A mixture of 6-aminophenanthridine (0.5 mmol), 1-bromo-2-phenylacetylene (0.6 mmol), $NaHCO_3$ (1 mmol), and DMF (0.5 mL) was heated at 120 °C for 24 h. The mixture was thenallowed to cool to room temperature, diluted with H_2O (15 mL) and then extracted with EtOAc (3 × 20 mL). The organic extracts were combined and then dried over anhydrous Na_2SO_4.

After evaporation of the solvent, the residue was purified by silica gel column chromatography to afford the corresponding product.

General Procedure for Intermediate C

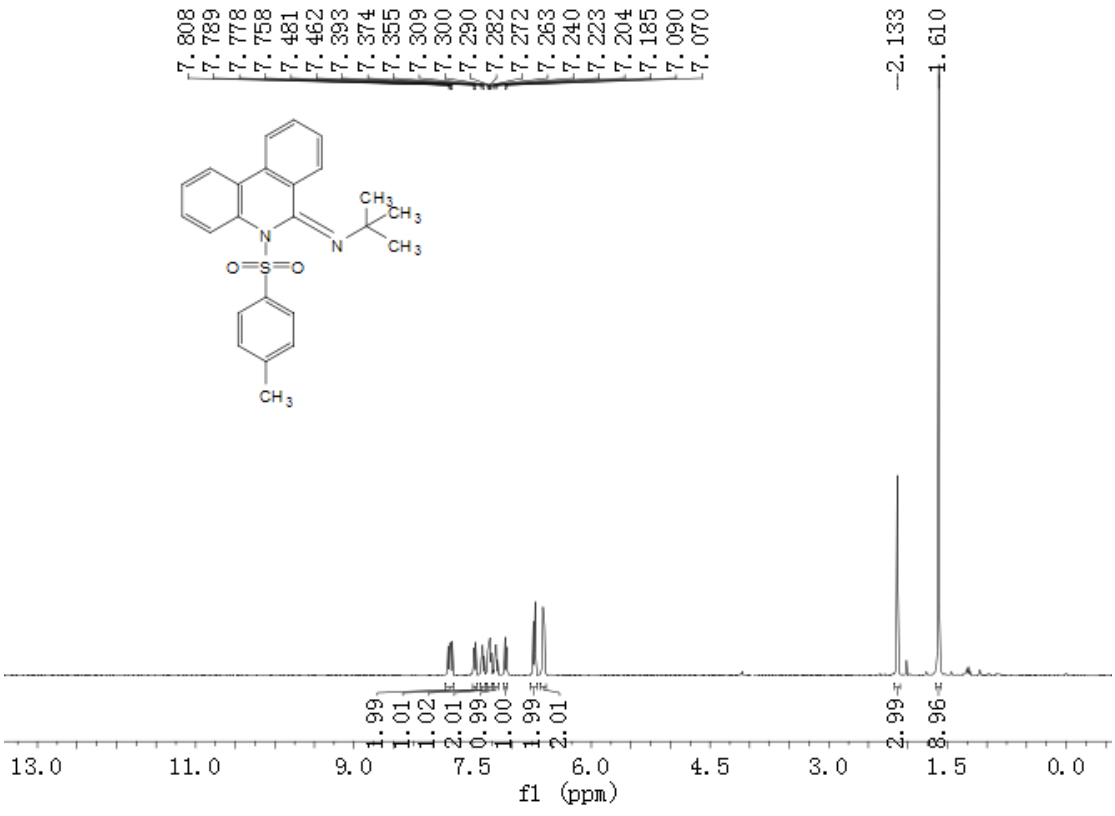


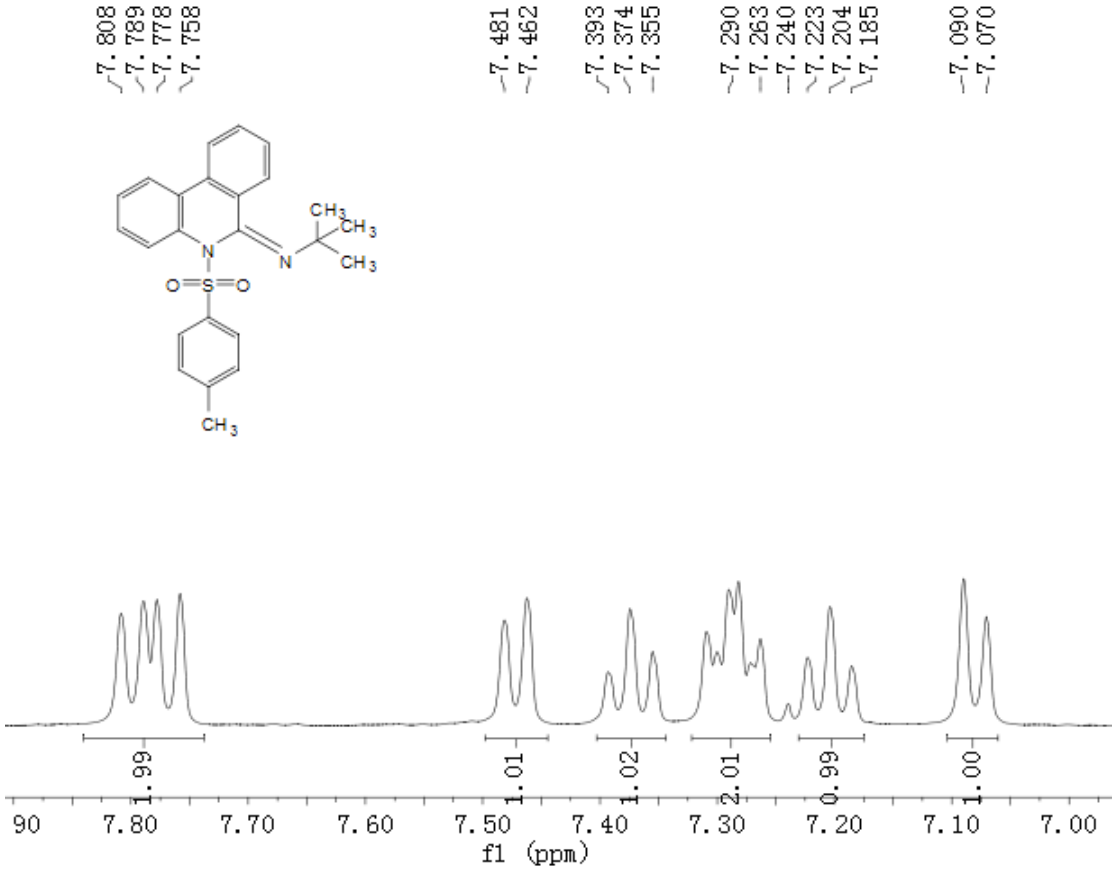
To a sealed tube *N*-sulfonyl-2-aminobiaryl (0.1 mmol), $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2$ (0.2 mmol), $NaHCO_3$ (0.2 mmol), H_2O (0.4 mmol) and DCE (2 mL) were added and stirred for three minutes at room temperature, then isocyanide (1.5 mmol) was added and stirred at 120 °C for 2 h. After cooling to room temperature, the mixture was extracted by ethyl acetate (3×10 mL), the organic layer was washed with brine, and dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was isolated by silica gel column chromatography, eluted with petroleum ether/ethyl acetate to give the pure product **C** in 60% yield. After stirring the intermediate **C** in the presence of $NaHCO_3$ (0.2 mmol) in DCE (2 mL) in a sealed tube for 10 h, product **3** could be obtained in 90% yield.

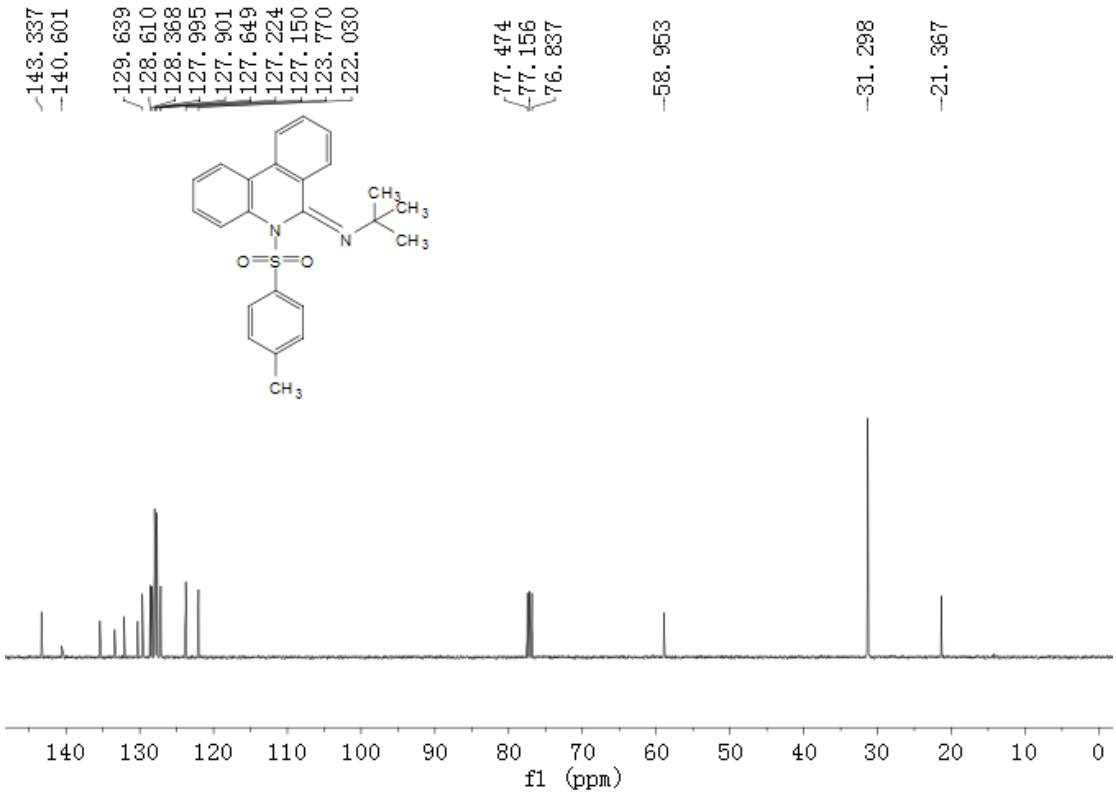


(E)-2-methyl-*N*-(5-tosylphenanthridin-6(5H)-ylidene)propan-2-amine (C): White solid; mp 148-152 °C. IR (KBr): 3071.1, 2962.7, 2924.3, 2864.8, 1766.1, 1350.8, 1089.9, 1031.6, 905.9, 810.9, 665.8, 619.0; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.70-8.68 (m, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.08 (s, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.60-7.52 (m, 2H), 7.50-7.44 (m, 3H), 7.39-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.5, 133.9, 131.5, 128.7, 128.7, 128.6, 128.4, 127.6, 127.4, 125.8, 124.9, 124.4, 124.0, 123.4, 122.2, 121.6, 115.6, 107.6; HRMS (ESI) m/z: calcd for $C_{24}H_{25}N_2O_2S^+$, 405.1631; found, 405.1629.

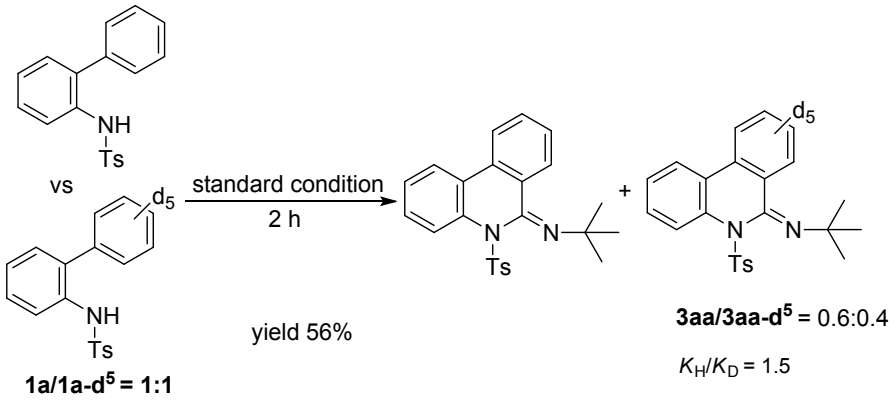
(E)-2-methyl-*N*-(5-tosylphenanthridin-6(5H)-ylidene)propan-2-amine (C)



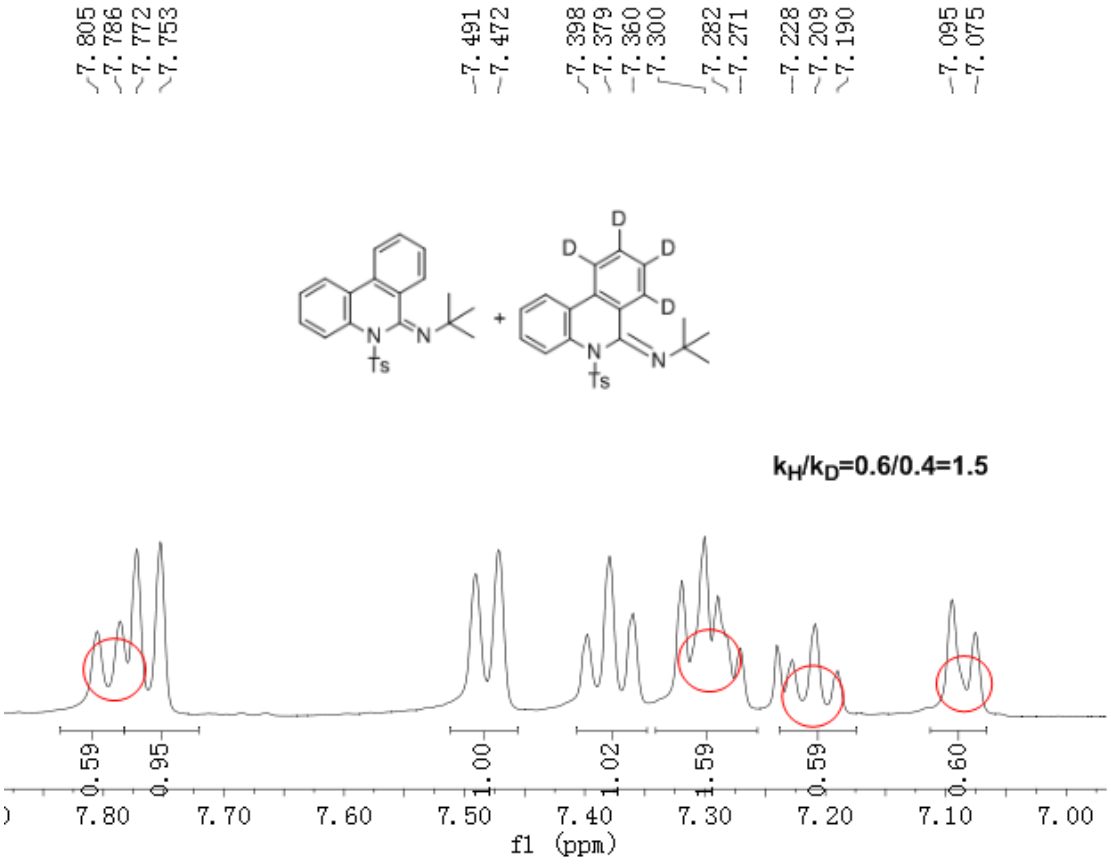

7.808
7.789
7.778
7.758
7.481
7.462
7.393
7.374
7.355
7.290
7.263
7.240
7.223
7.204
7.185
7.090
7.070
1.99
1.01
1.02
2.01
0.99
1.00
90
7.80
7.70
7.60
7.50
7.40
7.30
7.20
7.10
7.00
f1 (ppm)


143.337
140.601
129.639
128.610
128.368
127.995
127.901
127.649
127.224
127.150
123.770
122.030
77.474
77.156
76.837
58.953
31.298
21.367
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

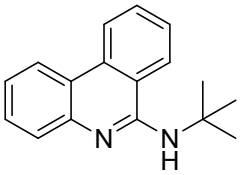
General Procedure for Kinetic Experiment and Kinetic Isotope Effects



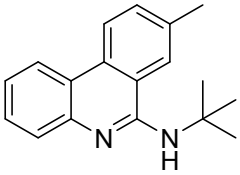
To a sealed tube *N*-sulfonyl-2-aminobiaryl (0.05 mmol), and substrate **1a-d$_5$** (0.05 mmol), $Pd(OAc)_2$ (10 mol %), $Cu(OAc)_2$ (0.2 mmol), $NaHCO_3$ (0.2 mmol), H_2O (0.4 mmol) and DCE (2 mL) were added and stirred for three minutes at room temperature, then isocyanide (1.5 mmol) was added and stirred at 120 °C for 2 h. After cooling to room temperature, the mixture was extracted by ethyl acetate (3×10 mL). The organic layer was washed with brine, and dried with anhydrous $MgSO_4$, filtered and concentrated under reduced pressure, and the residue was isolated by silica gel column chromatography, eluted with petroleum ether/ethyl acetate to give the corresponding product.



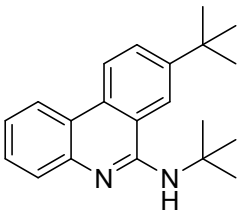
Analysis Data for Compounds 3aa-3ad, 4-5



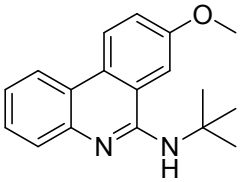
***N*-(*tert*-butyl)phenanthridin-6-amine (3aa)[5]:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.4 Hz, 1H), 8.34 (d, J = 8.0 Hz, 1H), 7.80-7.70 (m, 3H), 7.57 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 1H), 5.25 (br. s, 1H), 1.70 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 144.8, 133.9, 129.7, 128.7, 127.4, 126.8, 122.9, 122.3, 121.9, 121.8, 120.3, 119.7, 52.0, 29.4. LR-MS (EI, 70 eV): m/z = 250, 235, 194, 193, 151.



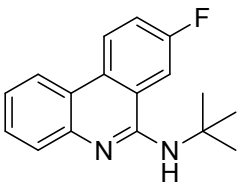
***N*-(*tert*-butyl)-8-methylphenanthridin-6-amine (3ba):** Brown solid; mp 83-88 ^{o}C. IR (KBr): 3743, 2987, 2360, 1764, 1242, 1055, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.4 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.54-7.49 (m, 3H), 7.28 (t, J = 7.6 Hz, 1H), 5.19 (br. s, 1H), 2.55 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 144.4, 136.6, 131.6, 131.2, 128.2, 127.3, 122.8, 122.2, 121.6, 121.5, 120.4, 119.8, 52.0, 29.4, 21.8. HRMS (ESI) m/z: calcd for $C_{18}H_{21}N_2^+$, 265.1699; found, 265.1694.



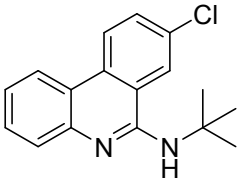
N,8-di-*tert*-butylphenanthridin-6-amine (3ca): Yellow oil. IR (KBr): 3592, 3437, 3381, 2961, 2034, 1630, 1093, 620; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 8.8 Hz, 1H), 8.29 (d, J = 7.6 Hz, 1H), 7.80-7.73 (m, 2H), 7.66 (d, J = 1.6 Hz, 1H), 7.52-7.48 (m, 1H), 7.30-7.26 (m, 2H), 5.17 (br. s, 1H), 1.67 (s, 9H), 1.44 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 149.7, 144.5, 131.6, 128.2, 127.9, 127.2, 122.7, 122.1, 121.6, 120.3, 119.4, 117.2, 52.0, 35.0, 31.4, 29.4. HRMS (ESI) m/z: calcd for $C_{21}H_{26}N_2^+$, 307.2169; found, 307.2165.



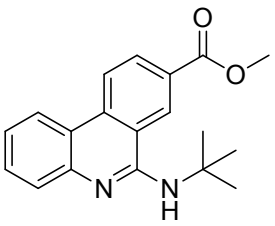
***N*-(*tert*-butyl)-8-methoxyphenanthridin-6-amine (3da):** Blackish green oil. IR (KBr): 3743, 2987, 2360, 1764, 1534, 1243, 1053, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.42 (d, J = 8.8 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 8.8 Hz, 1H), 7.48 (t, J = 8.0 Hz, 1H), 7.35-7.27 (m, 2H), 7.11 (s, 1H), 5.03 (br. s, 1H), 3.95 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.6, 151.7, 143.7, 127.9, 127.6, 127.3, 124.6, 122.4, 120.4, 118.4, 104.4, 55.7, 52.0, 29.4. HRMS (ESI) m/z: calcd for $C_{18}H_{21}N_2O^+$, 281.1648; found, 281.1645.



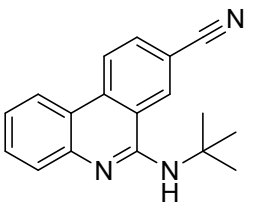
***N*-(*tert*-butyl)-8-fluorophenanthridin-6-amine (3ea):** Yellow solid; mp 98-105 °C. IR (KBr): 3743, 2963, 2369, 1745, 1536, 1236, 913, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50-8.46 (m, 1H), 8.26-8.23 (m, 1H), 7.77 (d, J = 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.47-7.39 (m, 2H), 7.35-7.28 (m, 1H), 5.01 (br. s, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.4 (d, J = 245.8 Hz), 151.5 (d, J = 3.2 Hz), 144.3, 130.5 (d, J = 2.0 Hz), 128.5, 127.5, 125.3 (d, J = 8.2 Hz), 122.6, 121.5, 120.9 (d, J = 6.6 Hz), 119.7 (d, J = 0.7 Hz), 118.4 (d, J = 23.0 Hz), 107.3 (d, J = 21.6 Hz), 52.2, 29.3. HRMS (ESI) m/z: calcd for $C_{17}H_{18}FN_2^+$, 269.1449; found, 269.1445.



***N*-(*tert*-butyl)-8-chlorophenanthridin-6-amine:** White solid; mp 156-162 °C. IR (KBr): 3745, 2920, 2361, 1740, 1527, 1215,913, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39 (d, J = 8.8 Hz, 1H), 8.23 (q, $J_1 = J_2$ = 0.8 Hz, 1H), 7.77-7.73 (m, 2H), 7.64 (q, $J_1 = J_2$ = 2 Hz, 1H), 7.56-7.52 (m, 1H), 7.32-7.28 (m, 1H), 5.10 (br. s, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.2, 144.6, 132.6, 132.4, 130.1, 129.0, 127.5, 124.6, 122.6, 121.6, 120.7, 119.5, 52.2, 29.3. HRMS (ESI) m/z: calcd for $C_{17}H_{18}ClN_2^+$, 285.1153; found, 285.1151.

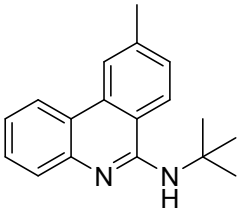


methyl 6-(*tert*-butylamino)phenanthridine-8-carboxylate (3ga): Yellow solid; mp 76-80 °C. IR (KBr): 3743, 2960, 2359, 1732, 1223, 913, 745; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, J = 8.4 Hz, 2H), 8.29 (d, J = 8.0 Hz, 2H), 7.75 (d, J = 6.8 Hz, 1H), 7.58-7.54 (m, 1H), 7.32-7.28 (m, 1H), 5.38 (br. s, 1H), 3.99 (s, 3H), 1.67 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.7, 152.3, 145.8, 137.3, 129.9, 129.5, 127.9, 127.5, 124.3, 123.0, 122.4, 119.5, 119.2, 52.4, 52.3, 29.3. HRMS (ESI) m/z: calcd for $C_{19}H_{21}N_2O_2^+$, 309.1598; found, 309.1599.

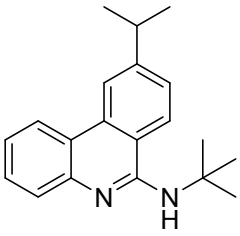


6-(*tert*-butylamino)phenanthridine-8-carbonitrile (3ha): Light yellow solid; mp 122-126.6 °C. IR (KBr): 3744, 3418, 2963, 2359, 1744, 1570, 1233, 1056, 744; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 8.0 Hz, 1H), 8.13 (d, J = 1.2 Hz, 1H), 7.86-7.83 (m, 1H), 7.75 (d, J = 8.0 Hz, 1H), 7.61-7.57 (m, 1H), 7.34-7.29 (m, 1H), 5.21 (br. s,

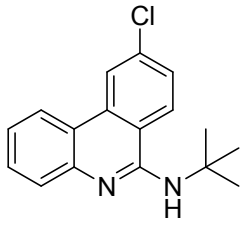
1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.1, 145.9, 137.0, 131.1, 130.5, 127.7, 127.6, 123.9, 123.0, 122.4, 119.4, 118.8, 118.8, 109.9, 52.5, 29.2. HRMS (ESI) m/z: calcd for $C_{18}H_{18}N_3^+$, 276.1495; found, 276.1491.



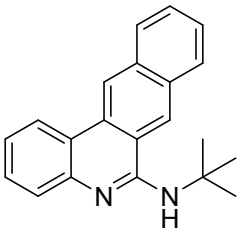
N-(*tert*-butyl)-9-methylphenanthridin-6-amine (3ia): Orange oil. IR (KBr): 3460, 2924, 1719, 1366, 1221, 913, 740; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31-8.28 (m, 2H), 7.76-7.74 (m, 1H), 7.65 (d, J = 8.4 Hz, 1H), 7.54-7.49 (m, 1H), 7.36 (q, $J_1 = J_2$ = 0.8 Hz, 1H), 7.30-7.26 (m, 1H), 5.18 (br. s, 1H), 2.57 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.4, 145.0, 139.7, 134.0, 128.5, 128.2, 127.3, 122.6, 122.0, 121.8, 121.7, 120.2, 117.7, 51.9, 29.4, 21.9. HRMS (ESI) m/z: calcd for $C_{18}H_{21}N_2^+$, 265.1699; found, 265.1697.



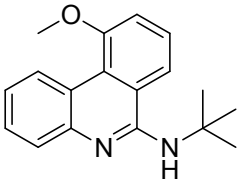
methyl N-(*tert*-butyl)-9-isopropylphenanthridin-6-amine (3ja): Yellow solid; mp 85-100 ^{o}C. IR (KBr): 3683, 3451, 2961, 1587, 1524, 1046, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (d, J = 8.4 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.72 (d, J = 8.4 Hz, 1H), 7.56-7.52 (m, 1H), 7.45 (q, $J_1 = J_2$ = 1.2 Hz, 1H), 7.34-7.30 (m, 1H), 5.24 (br. s, 1H), 3.20-3.10 (m, 1H), 1.68 (s, 9H), 1.39 (d, J = 6.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 149.4, 143.9, 132.9, 127.4, 126.3, 124.6, 121.0, 120.9, 120.6, 119.3, 118.9, 117.0, 50.9, 33.5, 28.4, 22.9. HRMS (ESI) m/z: calcd for $C_{20}H_{25}N_2^+$, 293.2012; found, 293.2013.



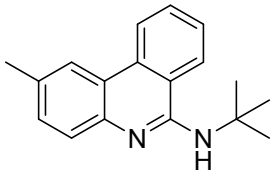
N-(*tert*-butyl)-9-chlorophenanthridin-6-amine (3ka): Yellow solid; mp 97-103 ^{o}C. IR (KBr): 3461, 2923, 1730, 1583, 1523, 1425, 1215, 754; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.43 (d, J = 1.6 Hz, 1H), 8.20 (d, J = 8.0 Hz, 1H), 7.76-7.68 (m, 2H), 7.54-7.47 (m, 2H), 7.32-7.28 (m, 1H), 5.14 (br. s, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 145.2, 136.1, 135.4, 129.3, 127.4, 127.0, 123.7, 122.5, 121.8, 119.2, 118.0, 116.5, 52.2, 29.3. HRMS (ESI) m/z: calcd for $C_{17}H_{18}ClN_2^+$, 285.1153; found, 285.1154.



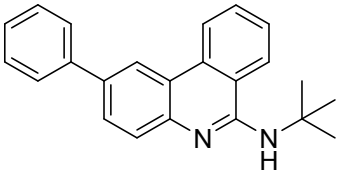
N-(*tert*-butyl)benzo[j]phenanthridin-6-amine (3la): Black oil. IR (KBr): 3708, 2965, 2866, 2359, 1554, 1420, 1010, 750; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.94 (s, 1H), 8.45 (d, J = 8.0 Hz, 1H), 8.27 (s, 1H), 8.04 (t, J = 8.4 Hz, 2H), 7.74 (d, J = 8.0 Hz, 1H), 7.61-7.50 (m, 1H), 7.34-7.30 (m, 1H), 5.43 (br. s, 1H), 1.72 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 144.3, 133.6, 131.6, 130.8, 128.8, 128.5, 128.0, 127.3, 126.1, 122.5, 122.0, 121.4, 120.4, 119.2, 119.7, 52.2, 29.4. HRMS (ESI) m/z: calcd for $C_{21}H_{21}N_2^+$, 301.1699; found, 301.1703.



***N*-(*tert*-butyl)phenanthridin-6-amine (3ma):** Blackish green oil IR (KBr): 3744, 2960, 2358, 1750, 1524, 1229, 1058, 913, 749; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.24 (q, J_1 = J_2 = 1.2 Hz, 1H), 7.78 (d, J = 8.0 Hz, 1H), 7.54-7.48 (m, 2H), 7.40 (d, J = 8.0 Hz, 1H), 7.31-7.27 (m, 1H), 7.20 (d, J = 7.6 Hz, 1H), 5.17 (br. s, 1H), 4.08 (s, 3H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.9, 152.1, 145.2, 128.0, 129.7, 127.8, 127.1, 127.0, 124.4, 122.1, 122.0, 120.0, 114.0, 111.1, 119.7, 55.8, 52.0, 29.4. HRMS (ESI) m/z: calcd for $C_{18}H_{21}N_2O^+$, 281.1648; found, 281.1656.

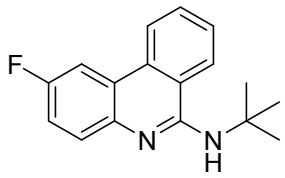


N-(*tert*-butyl)-2-methylphenanthridin-6-amine (3na): Black oil. IR (KBr): 3459, 2960, 2353, 1584, 1521, 1441, 1217, 721; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.50 (d, J = 8.4 Hz, 1H), 8.11 (s, 1H), 7.76 (d, J = 8.4 Hz, 1H), 7.71-7.66 (m, 2H), 7.56-7.52 (m, 1H), 7.36 (q, J_1 = J_2 = 1.6 Hz, 1H), 5.15 (br. s, 1H), 2.52 (s, 3H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.8, 142.8, 133.7, 131.5, 130.1, 129.4, 127.2, 126.6, 122.8, 121.9, 121.5, 120.0, 119.8, 51.9, 29.4, 21.6. HRMS (ESI) m/z: calcd for $C_{18}H_{21}N_2^+$, 265.1699; found, 265.1701.

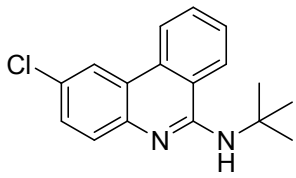


N-(*tert*-butyl)-2-phenylphenanthridin-6-amine (3oa): Yellow solid; mp 125-128 ^{o}C. IR (KBr): 3445, 2970, 2178, 2033, 1637, 1206, 1099, 620; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, J = 8.0 Hz, 1H), 8.55 (d, J = 8.0 Hz, 1H), 7.88-7.72 (m, 6H), 7.60-7.56 (m, 1H), 7.51 (t, J = 7.6 Hz, 2H), 7.38 (t, J = 7.2 Hz, 1H), 5.29 (br. s, 1H), 1.71 (s, 9H); ^{13}C NMR

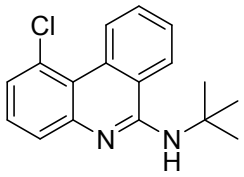
(100 MHz, $CDCl_3$) δ 152.4, 144.3, 141.8, 135.1, 134.0, 129.7, 128.9, 128.0, 127.8, 127.3, 126.9, 126.8, 122.9, 122.0, 120.3, 120.3, 119.9, 52.1, 29.4. HRMS (ESI) m/z: calcd for $C_{23}H_{23}N_2^+$, 327.1856; found, 327.1854.



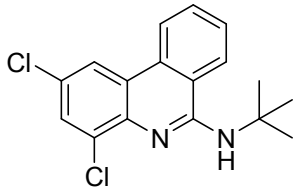
N-(*tert*-butyl)-2-fluorophenanthridin-6-amine (3pa): Black oil. IR (KBr): 3462, 3072, 2963, 2031, 1715, 1523, 1180, 620; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, J = 8.0 Hz, 1H), 7.85 (q, $J_1 = J_2$ = 2.8 Hz, 1H), 7.69 (d, J = 8.4 Hz, 1H), 7.65-7.62 (m, 2H), 7.53-7.51 (m, 1H), 7.21-7.17 (m, 1H), 5.11 (br. s, 1H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.7 (d, J = 238.4 Hz), 151.8, 141.4, 133.3 (d, J = 3.8 Hz), 132.4 (d, J = 74.9 Hz), 129.6 (d, J = 15.1 Hz), 128.9 (d, J = 8.3 Hz), 127.8 (d, J = 97.2 Hz), 123.0, 122.0, 120.9 (d, J = 6.6 Hz), 119.8, 116.9 (d, J = 23.5 Hz), 106.8 (d, J = 23 Hz), 52.0, 29.3. HRMS (ESI) m/z: calcd for $C_{17}H_{18}FN_2^+$, 269.1449; found, 269.1449.



N-(*tert*-butyl)-2-chlorophenanthridin-6-amine (3qa): Yellow solid; mp 107-113 ^{o}C. IR (KBr): 3463, 2958, 1583, 1520, 1216, 1089, 716; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.38 (d, J = 8.0 Hz, 1H), 8.23 (d, J = 2.0 Hz, 1H), 7.76-7.65 (m, 3H), 7.57 (t, J = 7.6 Hz, 1H), 7.44 (q, $J_1 = J_2$ = 2.0 Hz, 1H), 5.25 (br. s, 1H), 1.64 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 143.3, 132.9, 129.9, 128.9, 128.7, 127.4, 127.4, 122.9, 121.9, 121.4, 121.2, 119.7, 52.1, 29.3. HRMS (ESI) m/z: calcd for $C_{17}H_{18}ClN_2^+$, 285.1153; found, 285.1147.

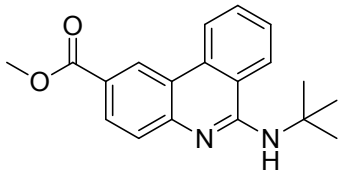


N-(*tert*-butyl)-1-chlorophenanthridin-6-amine (3ra): Black solid; mp 110-117 ^{o}C. IR (KBr): 3466, 2967, 2032, 1639, 1209, 1098, 620; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 8.11 (d, J = 8.8 Hz, 1H), 7.68-7.61 (m, 3H), 7.51-7.46 (m, 1H), 7.17-7.14 (m, 1H), 5.23 (br. s, 1H), 1.57 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.9, 145.7, 134.1, 133.4, 130.0, 127.0, 126.4, 123.0, 122.8, 122.5, 121.9, 119.5, 118.8, 52.2, 29.3. HRMS (ESI) m/z: calcd for $C_{17}H_{18}ClN_2^+$, 285.1153; found, 285.1152.

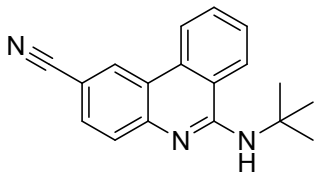


N-(*tert*-butyl)-2,4-dichlorophenanthridin-6-amine (3sa): Yellow

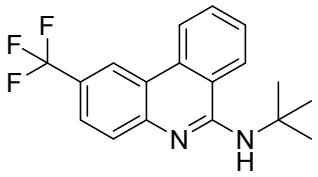
solid; mp 100-112 °C. IR (KBr): 3707, 2966, 2867, 2359, 1354, 1056, 1012; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34 (d, J = 8.4 Hz, 1H), 8.12 (d, J = 2.0 Hz, 1H), 7.76-7.70 (m, 2H), 7.62-7.58 (m, 2H), 5.39 (br. s, 1H), 1.69 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.3, 139.9, 132.7, 132.2, 130.2, 128.8, 127.9, 126.4, 123.2, 122.1, 121.9, 120.2, 119.6, 52.4, 28.8. HRMS (ESI) m/z: calcd for $C_{17}H_{17}Cl_2N_2^+$, 319.0763; found, 319.0752.



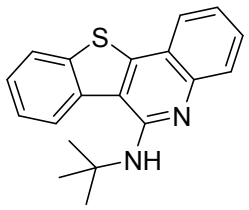
methyl 6-(*tert*-butylamino)phenanthridine-2-carboxylate (3ta): Yellow solid; mp 82-90 °C. IR (KBr): 3430, 2982, 1763, 1530, 1239, 913, 741; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.04 (d, J = 1.6 Hz, 1H), 8.58 (d, J = 8.4 Hz, 1H), 8.15-8.12 (m, 1H), 7.77-7.72 (m, 3H), 7.60-7.56 (m, 1H), 5.46 (br. s, 1H), 1.66 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 167.6, 153.7, 148.2, 133.8, 130.2, 129.1, 127.3, 127.1, 124.7, 123.3, 123.1, 121.9, 119.6, 119.6, 52.4, 52.0, 29.3. HRMS (ESI) m/z: calcd for $C_{19}H_{21}N_2O_2^+$, 309.1598; found, 309.1598.



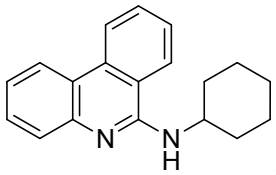
6-(*tert*-butylamino)phenanthridine-2-carbonitrile (3ua): Yellow solid; mp 120-126 °C. IR (KBr): 3706, 2935, 2357, 1536, 1051, 1011, 681; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, J = 1.6 Hz, 1H), 8.40 (d, J = 8.0 Hz, 1H), 7.78-7.75 (m, 2H), 7.72-7.61 (m, 3H), 5.52 (br. s, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.9, 147.5, 132.7, 130.7, 130.6, 130.0, 128.0, 127.4, 126.5, 122.8, 122.0, 120.3, 119.7, 104.5, 52.6, 29.2. HRMS (ESI) m/z: calcd for $C_{18}H_{18}N_3$+, 276.1495; found, 276.1488.



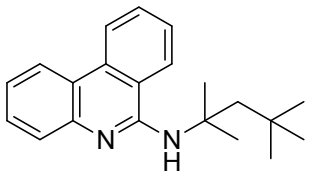
N-(*tert*-butyl)-2-(trifluoromethyl)phenanthridin-6-amine (3va): Yellow solid; mp 110-125.6 °C. IR (KBr): 3469, 2964, 2033, 1529, 1309, 1105, 1019, 622; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (s, 1H), 8.50 (d, J = 8.0 Hz, 1H), 7.80-7.74 (m, 3H), 7.71-7.68 (m,1H), 7.63-7.59 (m, 1H), 7.33 (t, J = 7.6 Hz, 1H), 5.40 (br. s, 1H), 1.65 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.5, 146.8, 133.4, 130.2, 127.7, 127.6, 126.3, 125.0 (q, J = 269.8 Hz), 124.7 (q, J = 3.3 Hz), 123.7 (q, J = 31.8 Hz), 122.9, 121.9, 119.8, 119.6, 119.5 (q, J = 4.2 Hz), 52.3, 29.2. HRMS (ESI) m/z: calcd for $C_{18}H_{18}F_3N_2^+$, 319.1417; found, 319.1413.



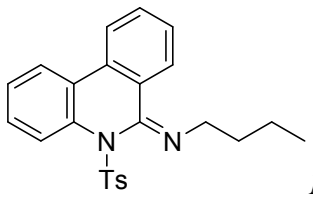
***N*-(*tert*-butyl)benzo[4,5]thieno[3,2-c]quinolin-6-amine (3wa):** Brown solid; mp 88-95 °C. IR (KBr): 3739, 2962, 2357, 1740, 1564, 1515, 1223, 747; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 (d, *J* = 8.0 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.91-7.85 (m, 2H), 7.60-7.52 (m,2H), 7.49-7.44 (m, 1H), 7.31-7.28 (m, 1H), 5.32 (br. s, 1H), 1.74 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.6, 147.0, 145.2, 139.0, 134.9, 129.3, 127.3, 125.3, 125.2, 123.6, 123.4, 122.3, 122.1, 119.7, 118.4, 52.5, 29.5. HRMS (ESI) m/z: calcd for $C_{19}H_{19}N_2S^+$, 307.1263; found, 307.1262.



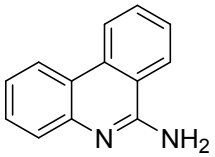
***N*-cyclohexylphenanthridin-6-amine (3ab)[5]:** ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.50 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.0 Hz, 1H), 7.84-7.81 (m, 2H), 7.74-7.70 (m, 1H), 7.60-7.54 (m, 2H), 7.35-7.31 (m, 1H), 5.26 (br. s, 1H), 4.77–4.39 (m, 1 H), 2.73–2.36 (m, 2 H), 1.84–1.70 (m, 3 H), 1.61–1.50 (m, 2 H), 1.36–1.27 (m, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.2, 145.0, 133.9, 129.8, 128.7, 126.9, 126.7, 122.7, 122.1, 121.7, 120.4, 119.2, 49.2, 33.3, 25.9, 25.0. LR-MS (EI, 70 eV): m/z = 276, 219, 194, 178.



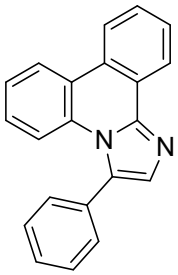
***N*-(2,4,4-trimethylpentan-2-yl)phenanthridin-6-amine (3ac) [5]:** ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.0 Hz, 1H), 8.40 (d, *J* = 8.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.75 (t, *J* = 8.0 Hz, 1H), 7.67-7.59 (m, 2H), 7.42-7.38 (m, 1H), 5.36 (br. s, 1H), 2.27 (s, 2H), 1.84 (s, 6H), 1.16 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.0, 144.8, 133.8, 129.5, 128.5, 127.3, 126.7, 122.8, 122.0, 121.7, 121.6, 120.1, 119.7, 55.8, 51.6, 31.8, 31.7, 29.8. LR-MS (EI, 70 eV): m/z = 306, 280, 235, 194, 178.



***N*-butyl-5-tosyl-5,6-dihydrophenanthridin-6-amine (3ad)**: Brown oil. IR (KBr): 3068.2, 2969.7, 2862.0, 1916.0, 1736.3, 1597.8, 1484.4, 1356.9, 924.0, 768.5, 668.1, 581.5, 545.2; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.0 Hz, 1H), 8.62-8.56 (m, 2H), 7.90-7.85 (m, 2H), 7.80-7.76 (m, 1H), 7.69-7.67 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 3.72-3.70 (m, 2H), 2.45 (s, 3H), 1.31-1.26 (m, 4H), 0.78-0.74 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.7, 143.6, 143.0, 134.8, 134.6, 131.3, 129.7, 129.2, 128.7, 128.2, 127.6, 127.1, 124.6, 122.2 121.7, 50.5, 30.3, 21.6, 20.1, 13.6. HRMS (ESI) m/z: calcd for $C_{24}H_{25}N_2O_2S^+$, 405.1631; found, 405.1630.



phenanthridin-6-amine (4)[6]: ^{1}H NMR (400 MHz, $(CD_3)_2C=O$) δ 7.52 (d, J = 8.4 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.19 (d, J = 8.0 Hz, 1H), 6.71-6.67 (m, 1H), 6.55-6.49 (m, 2H), 6.40-6.36 (m, 1H), 6.19-6.15 (m, 1H), 5.56 (br. s, 2H); ^{13}C NMR (100 MHz, $(CD_3)_2C=O$) δ 156.5, 146.0, 134.9, 131.5, 129.5, 127.9, 127.1, 125.1, 123.4, 123.2, 123.0, 121.8, 119.9. LR-MS (EI, 70 eV): m/z = 194, 178, 166, 139.



3-phenylimidazo[1,2-f]phenanthridine (5): Yellow solid; mp 143-146 ^{o}C. IR (KBr): 3058.2, 2969.7, 2962.0, 2028.1, 1664.4, 1434.7, 1163.8, 1097.6, 754.1, 621.3; ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.70-8.68 (m, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.21 (d, J = 7.6 Hz, 1H), 8.08 (s, 1H), 8.02 (d, J = 8.0 Hz, 2H), 7.70 (d, J = 8.0 Hz, 1H), 7.60-7.52 (m, 2H), 7.50-7.44 (m, 3H), 7.39-7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.9, 142.5, 133.9, 131.5, 128.7, 128.7, 128.6, 128.4, 127.6, 127.4, 125.8, 124.9, 124.4, 124.0, 123.4, 122.2, 121.6, 115.6, 107.6; HRMS (ESI) m/z: calcd for $C_{21}H_{15}N_2^+$, 295.1230; found, 295.1233.

Reference

[1] S. W. Youn, J. H. Bihn, B. S. Kim, *Org. Lett.;* 2011, **13**, 3738.

[2] P. P. Sharp, M. G. Banwell, J. Renner, K. Lohmann, A. C. Willis, *Org. Lett;,* 2013, **15**, 2616.

[3] S. Santra, A. K. Bagdi, A. Majee, A. Hajra, *Adv. Synth. Catal*.; 2013, **355**, 1065.

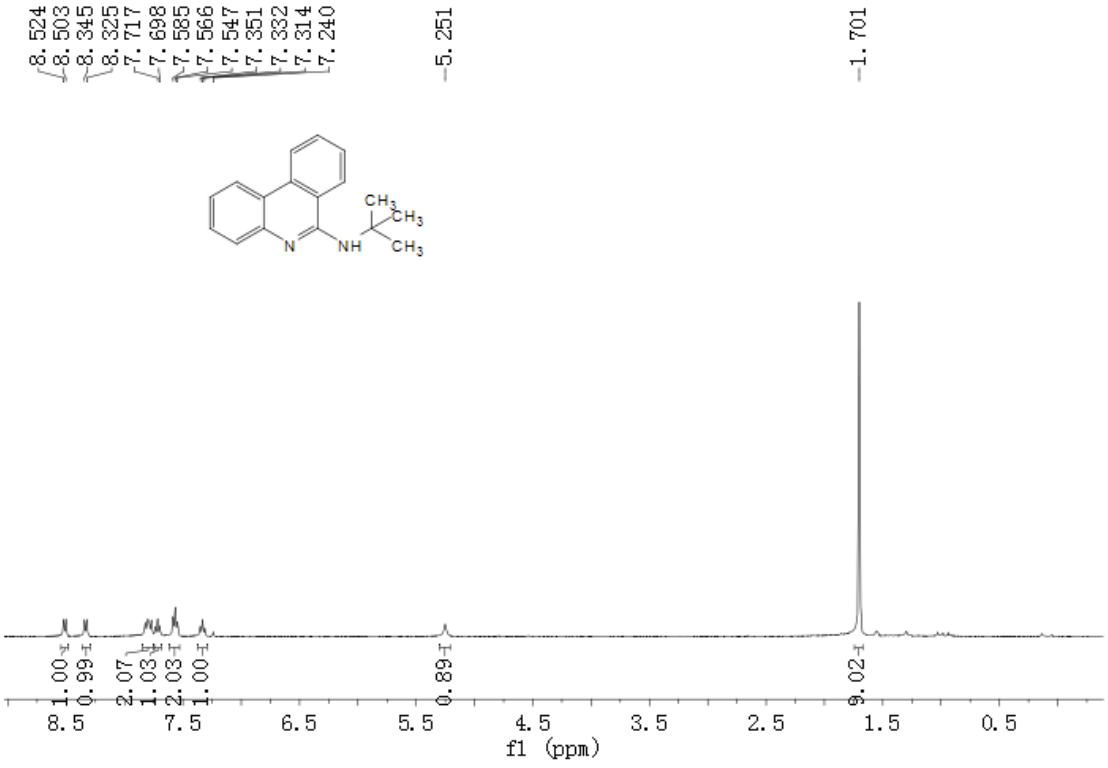
[4] Z. Q. Wu, Y. Y. Pan, X. G. Zhou, *Synthesis.;* 2011, **14**, 2255.

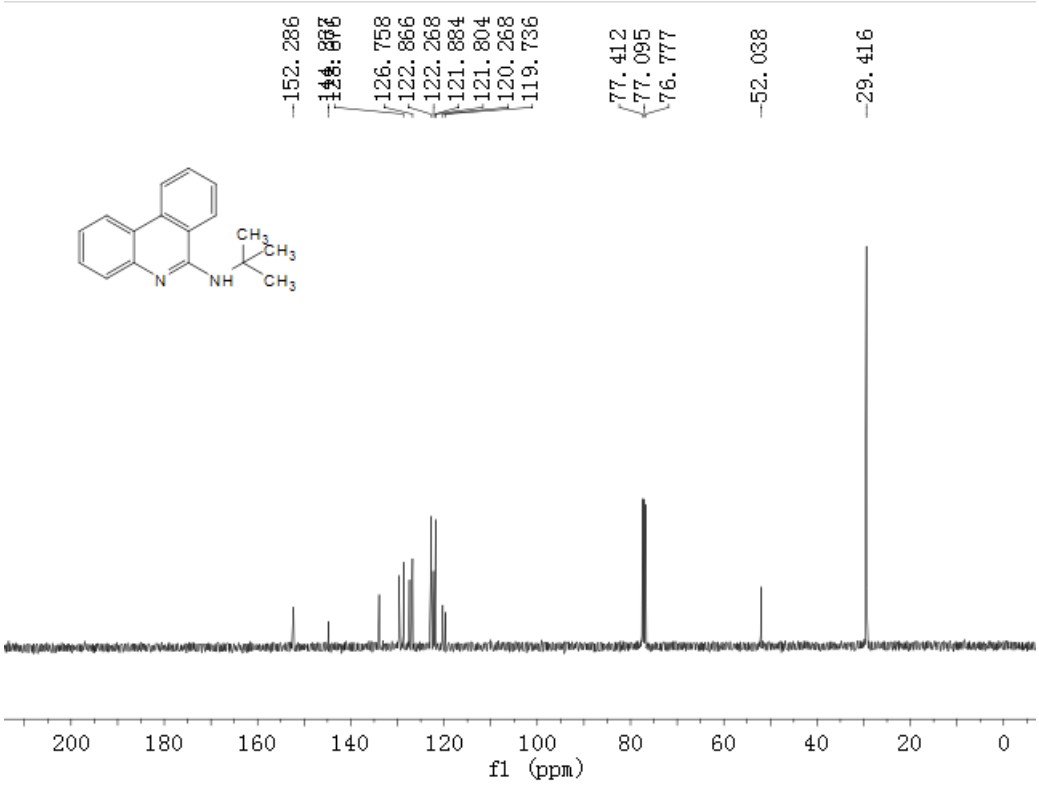
[5] B. F. Liu, Y. B. Li, M. Z. Yin, H. W. Huang, H. F. Jiang, *Adv. Synth. Catal.;* 2012, **354**, 2288.

[6] F. Gug, M. Blondel, N. Desban, S. Bouaziz, J-M. Vierfond, H. Galons, *Tetrahedron Lett.;* 2005, **46**, 3725.

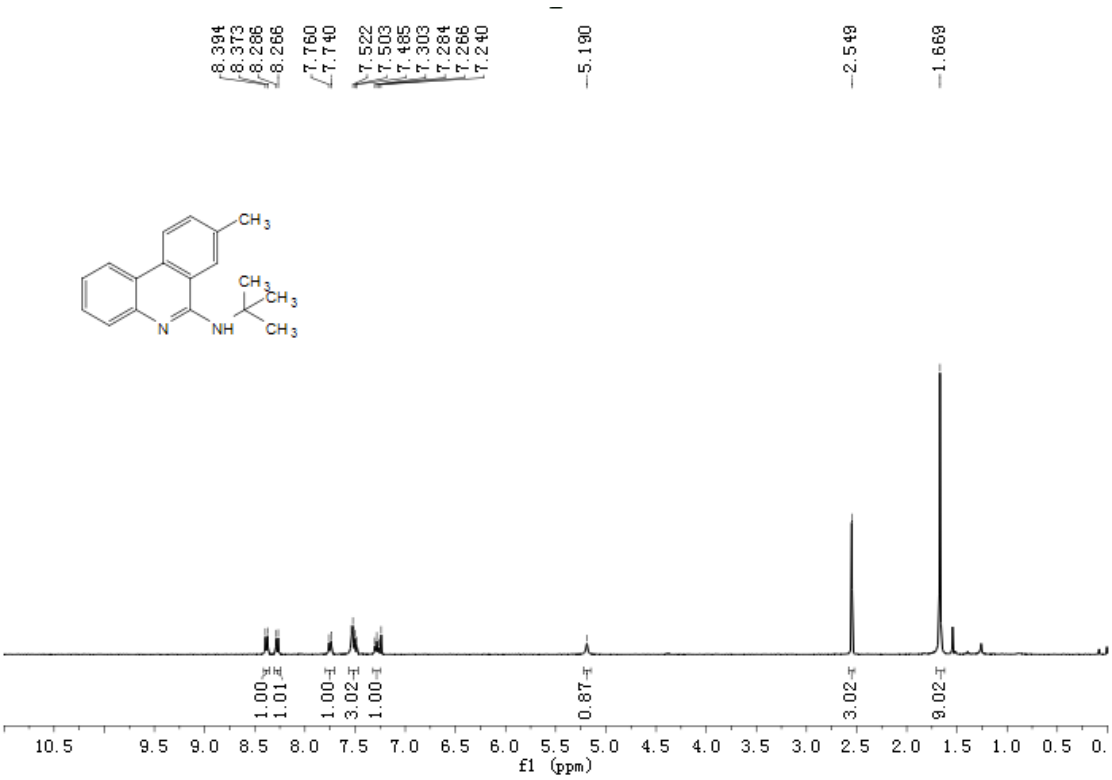
NMR Spectra for Compounds 3aa-3ad, 4-5

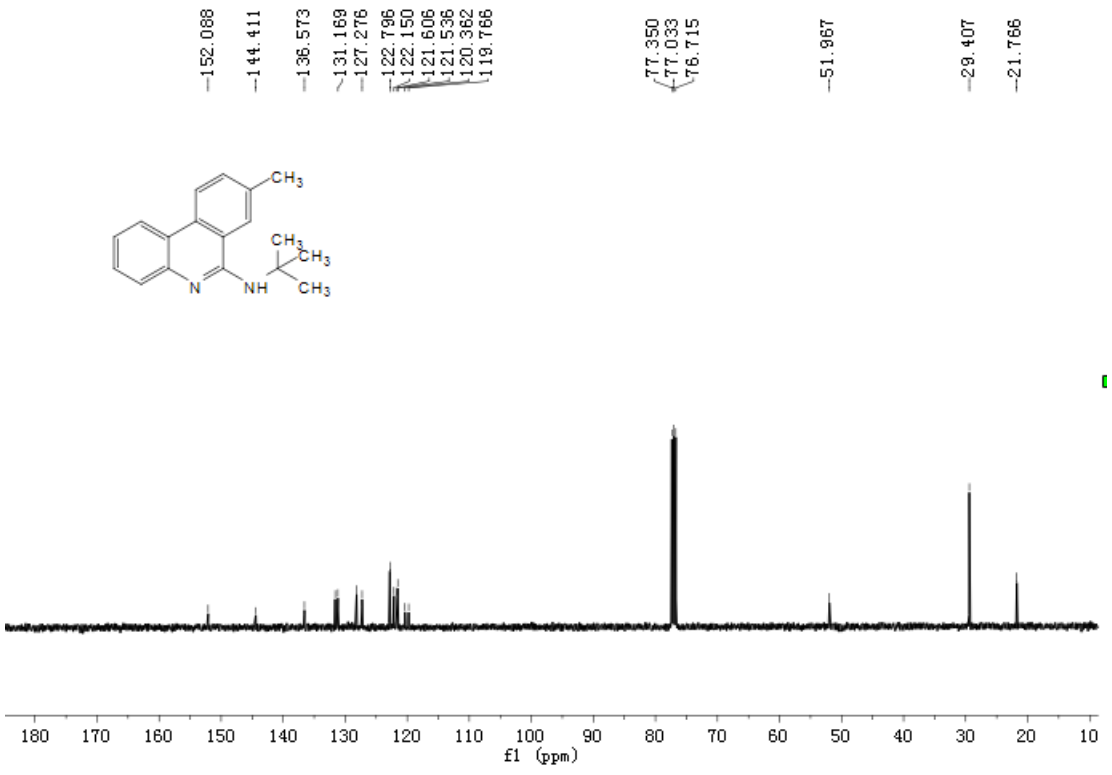
***N*-(*tert*-butyl)phenanthridin-6-amine (3aa)**



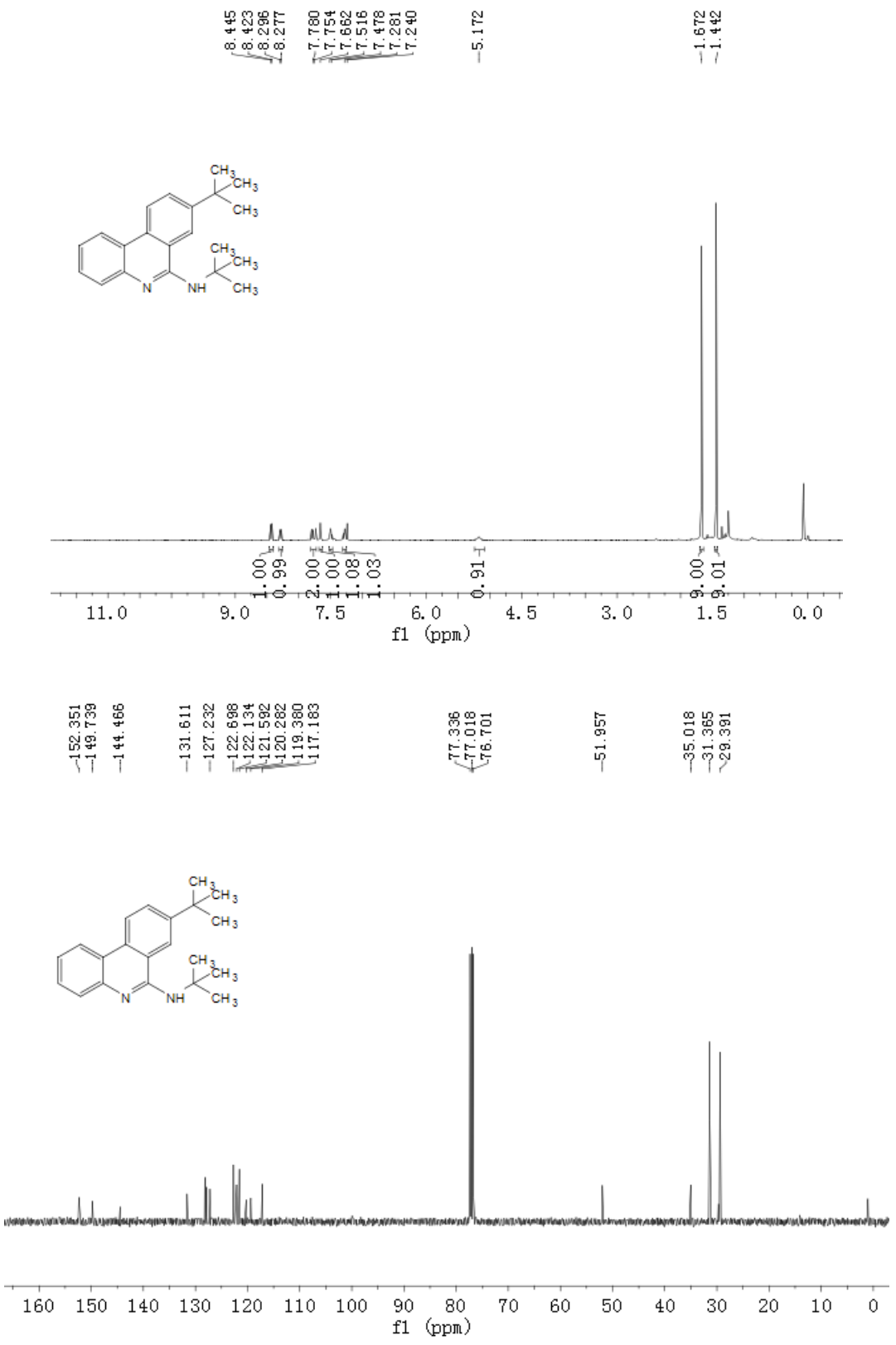


***N*-(*tert*-butyl)-8-methylphenanthridin-6-amine（3ba）**

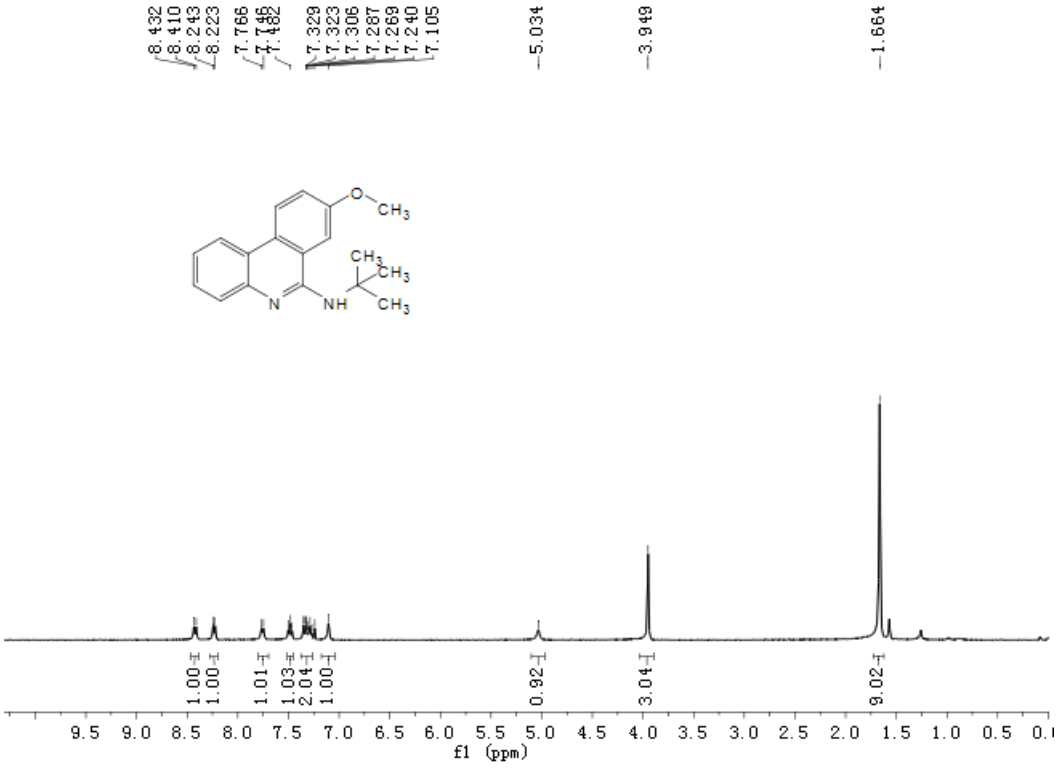


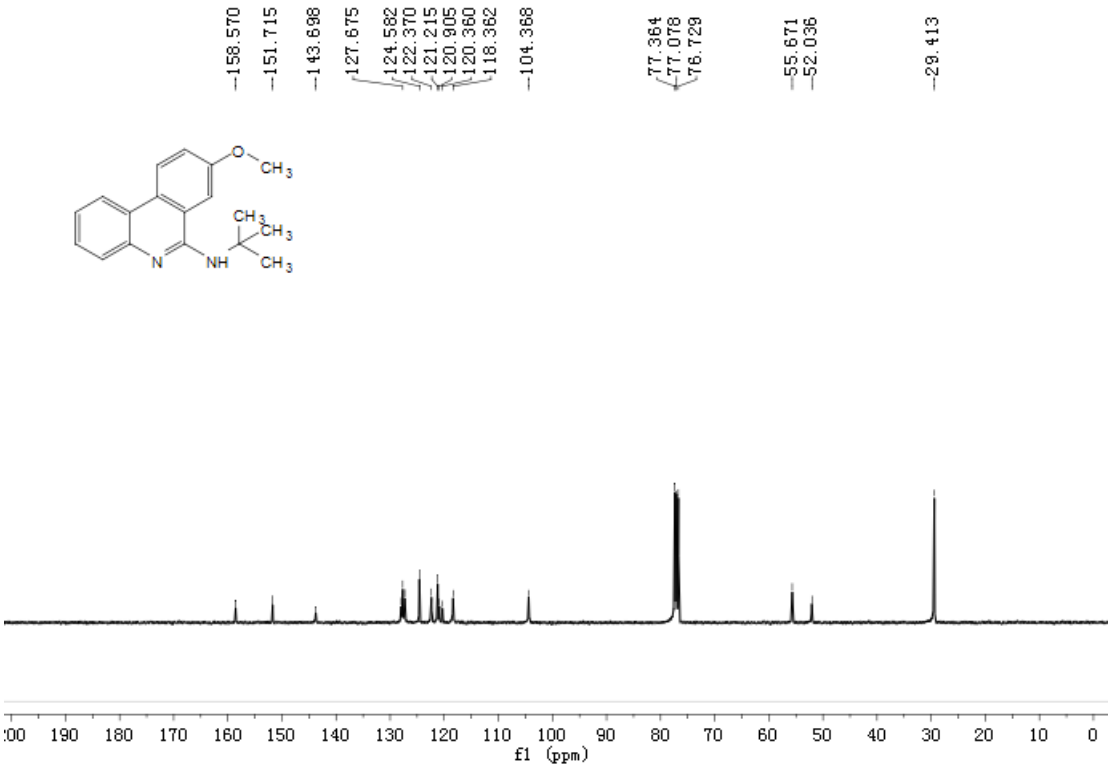


***N*,8-di-tert-butylphenanthridin-6-amine (3ca)**

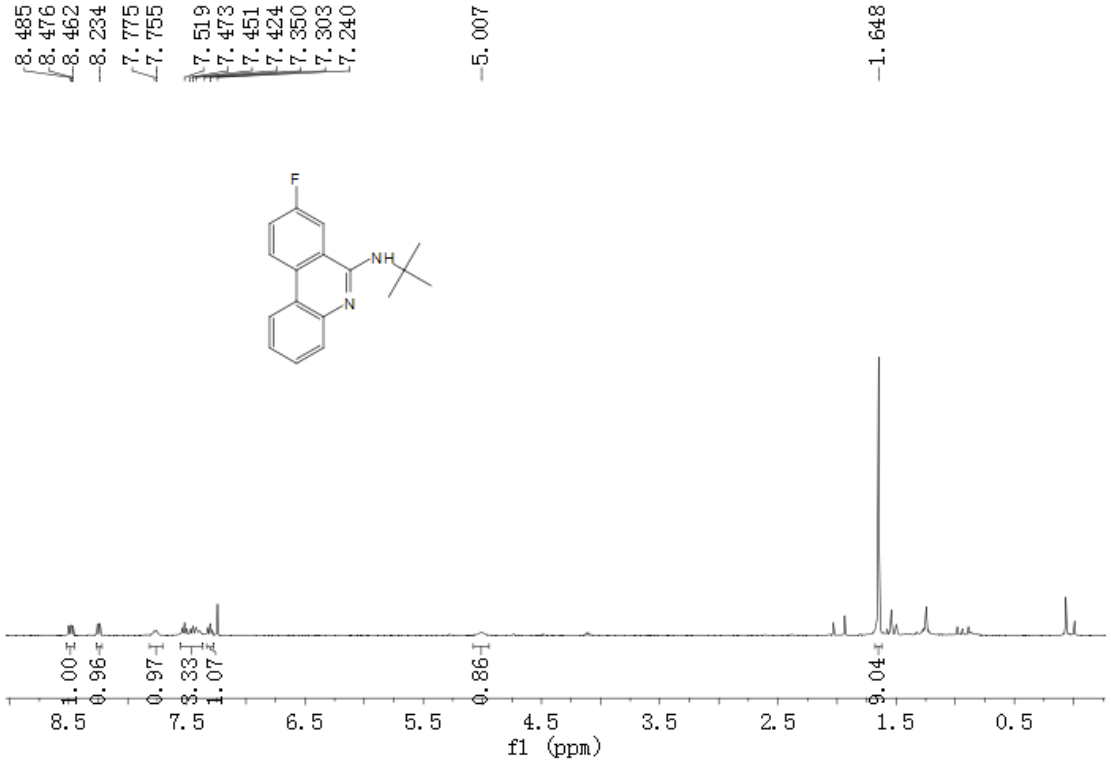


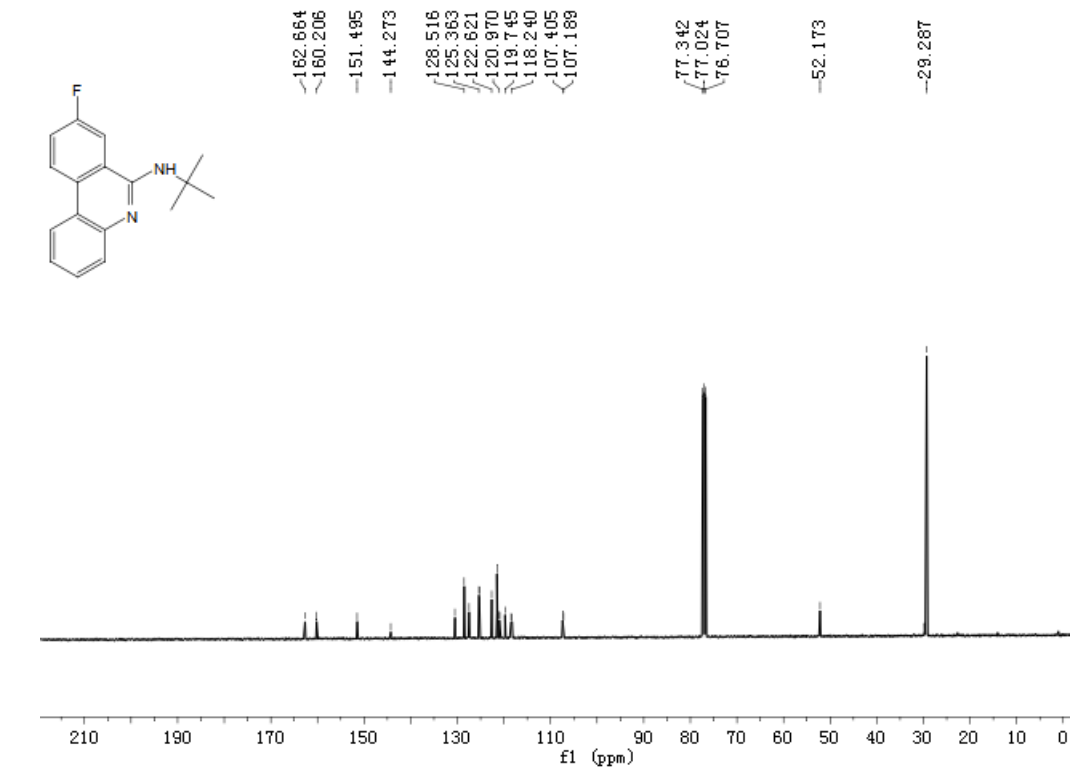
***N*-(*tert*-butyl)-8-methoxyphenanthridin-6-amine（3da）**



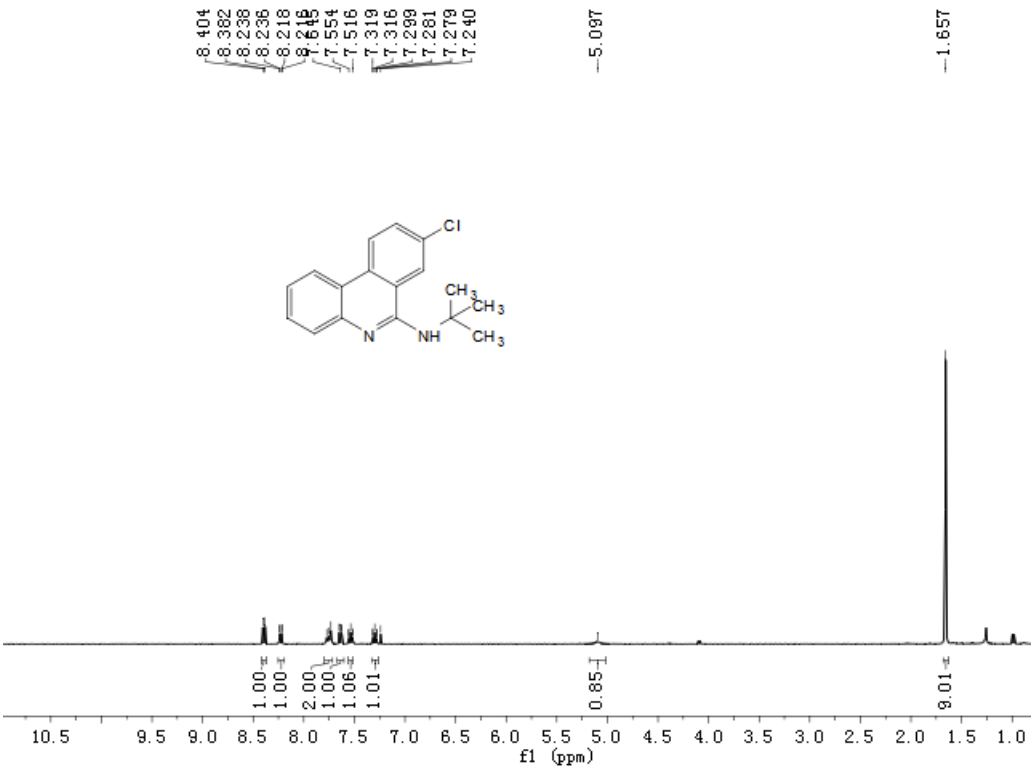


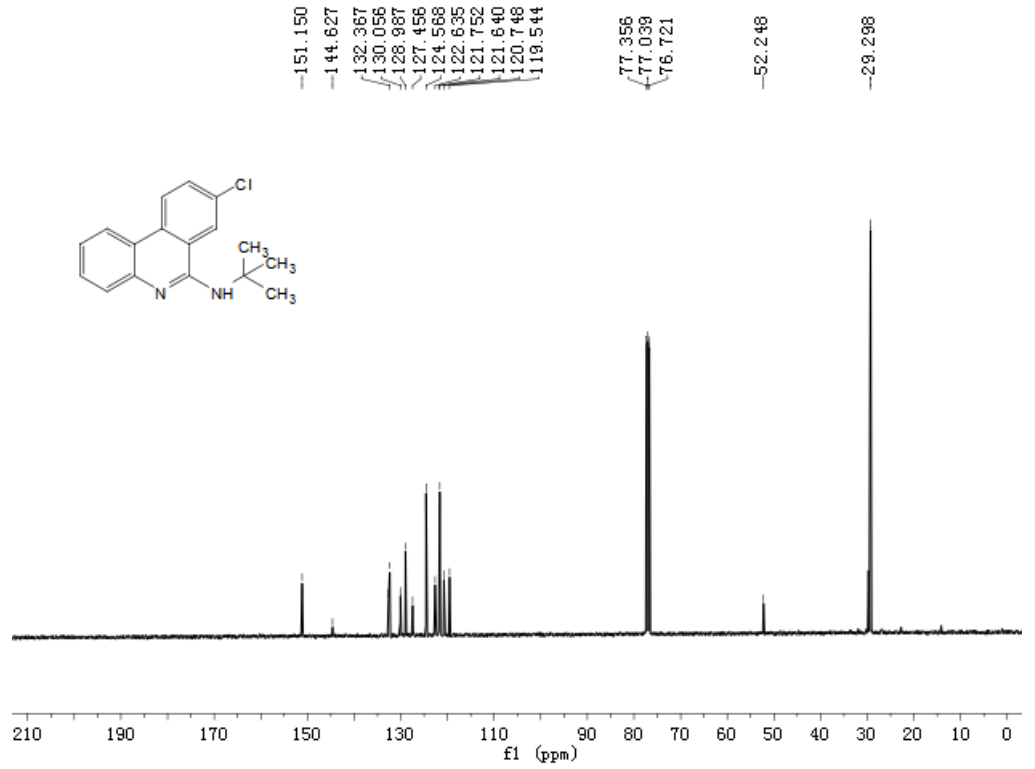
***N*-(*tert*-butyl)-8-fluorophenanthridin-6-amine（3ea）**



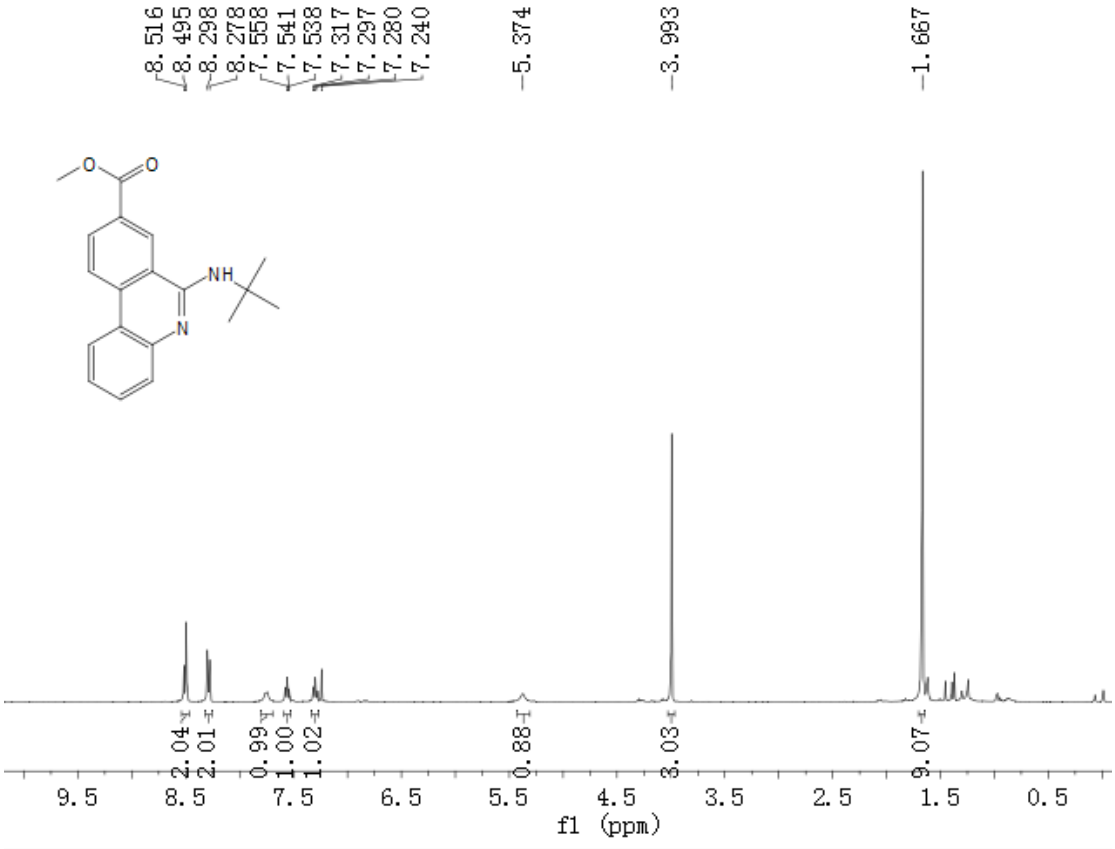


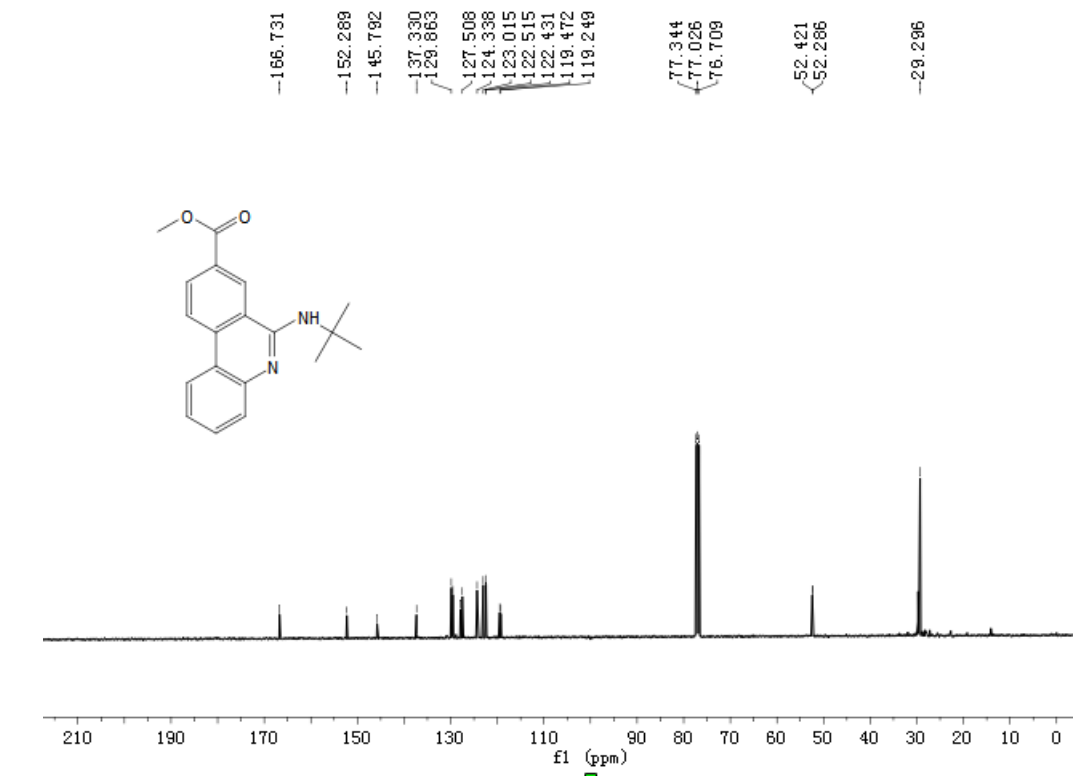
***N*-(*tert*-butyl)-8-chlorophenanthridin-6-amine（3fa）**



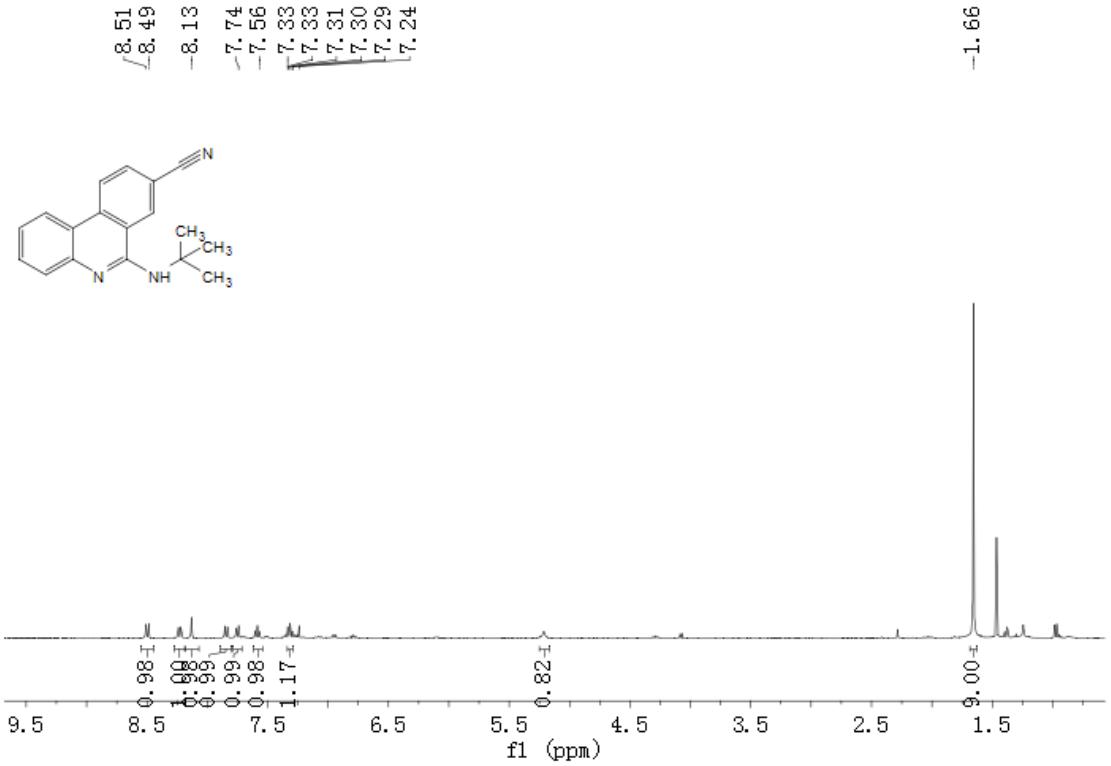


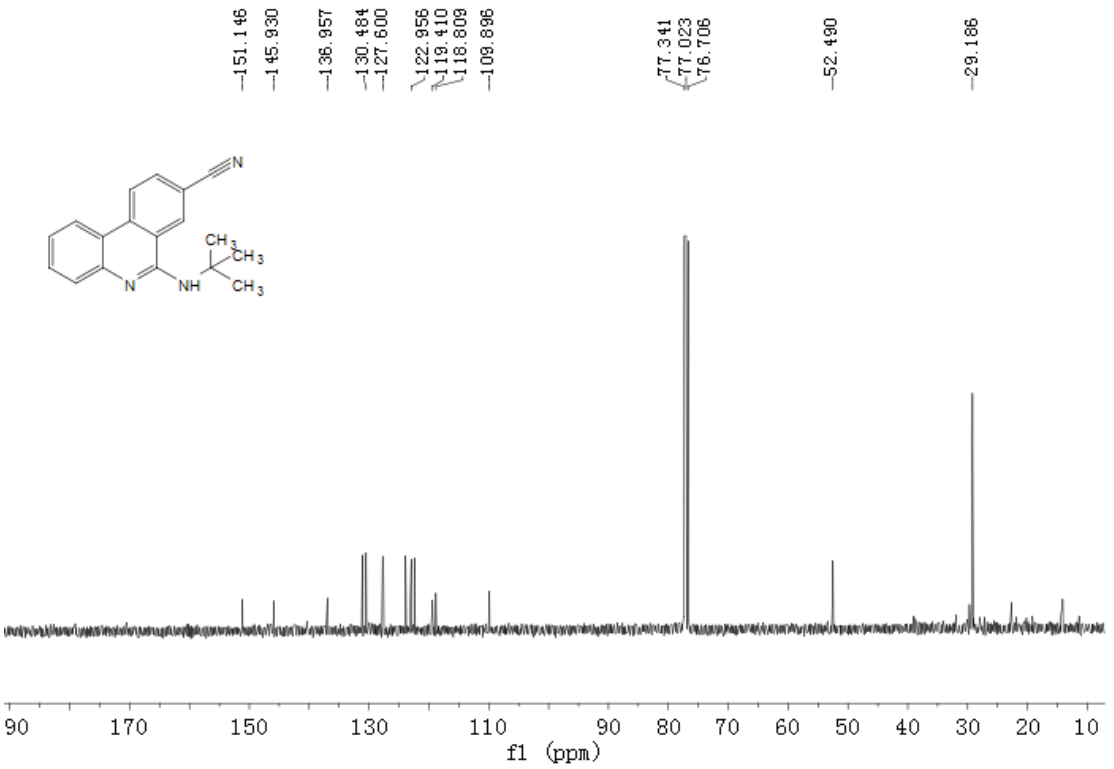
methyl 6-(*tert*-butylamino)phenanthridine-8-carboxylate（3ga）



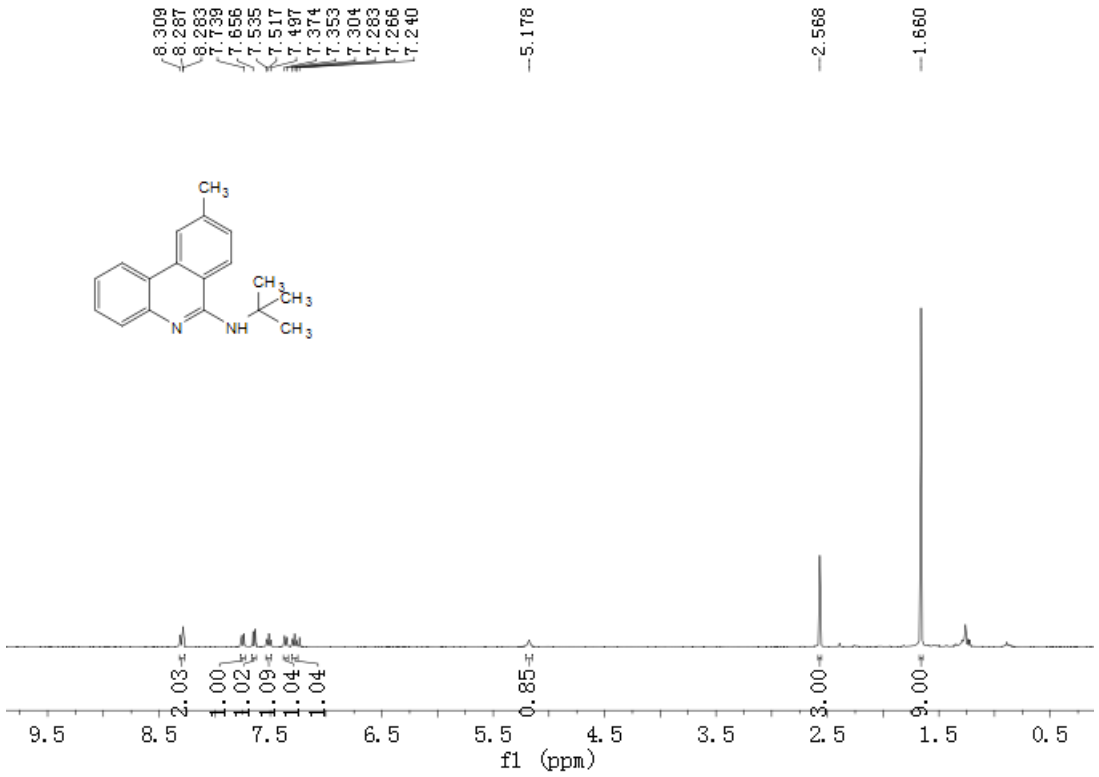


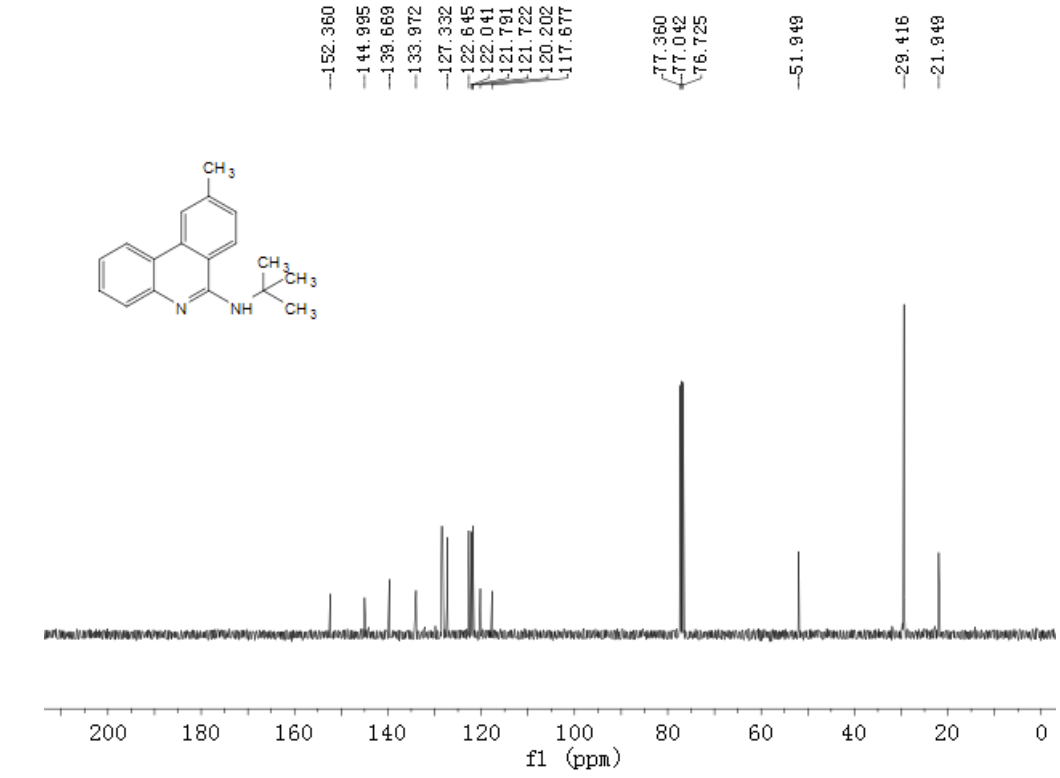
6-(*tert*-butylamino)phenanthridine-8-carbonitrile（3ha）





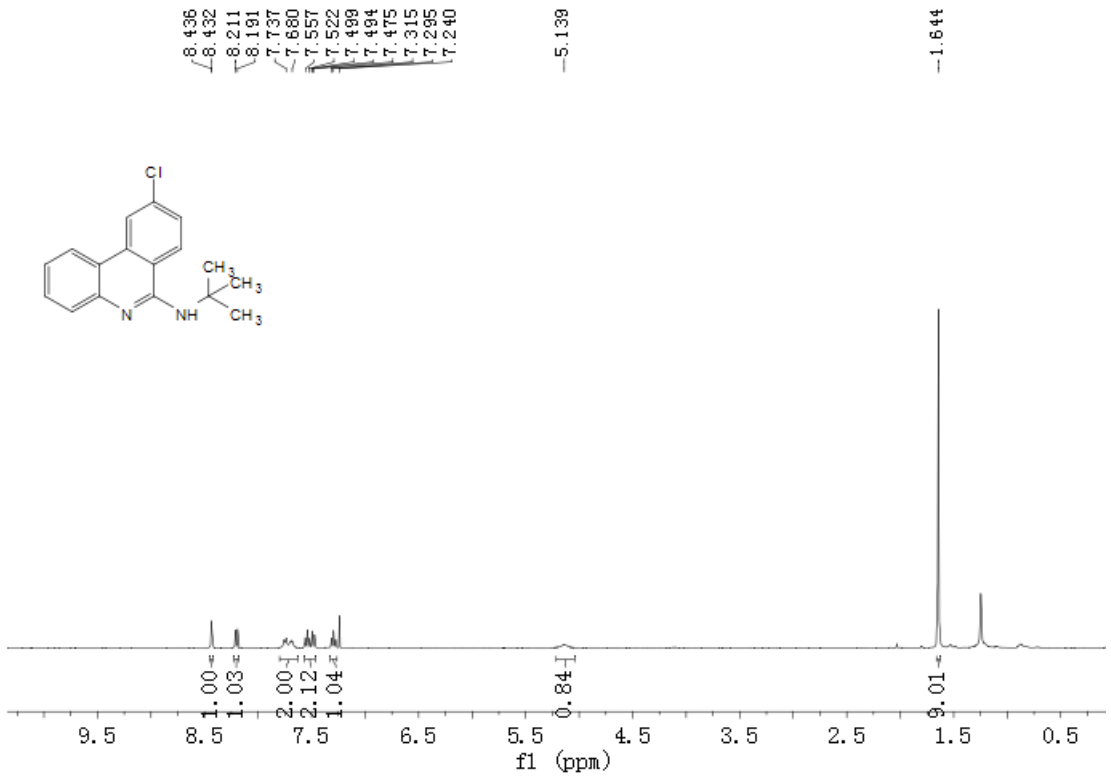
***N*-(tert-butyl)-9-methylphenanthridin-6-amine（3ia）**

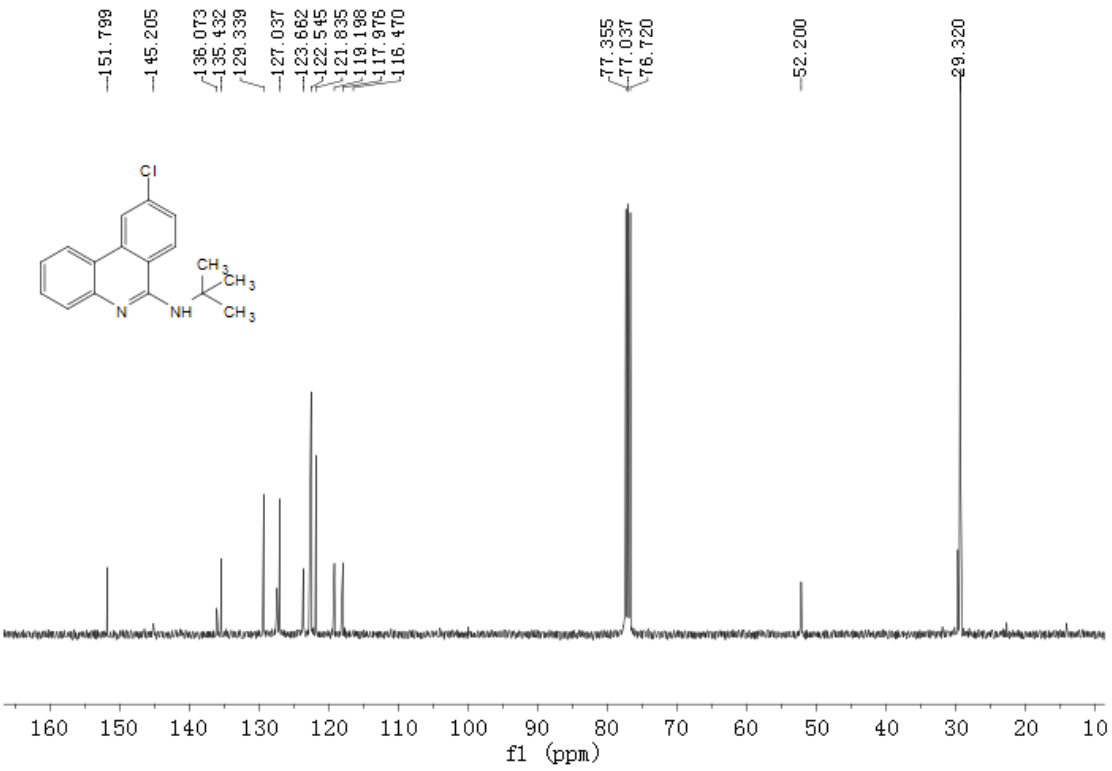




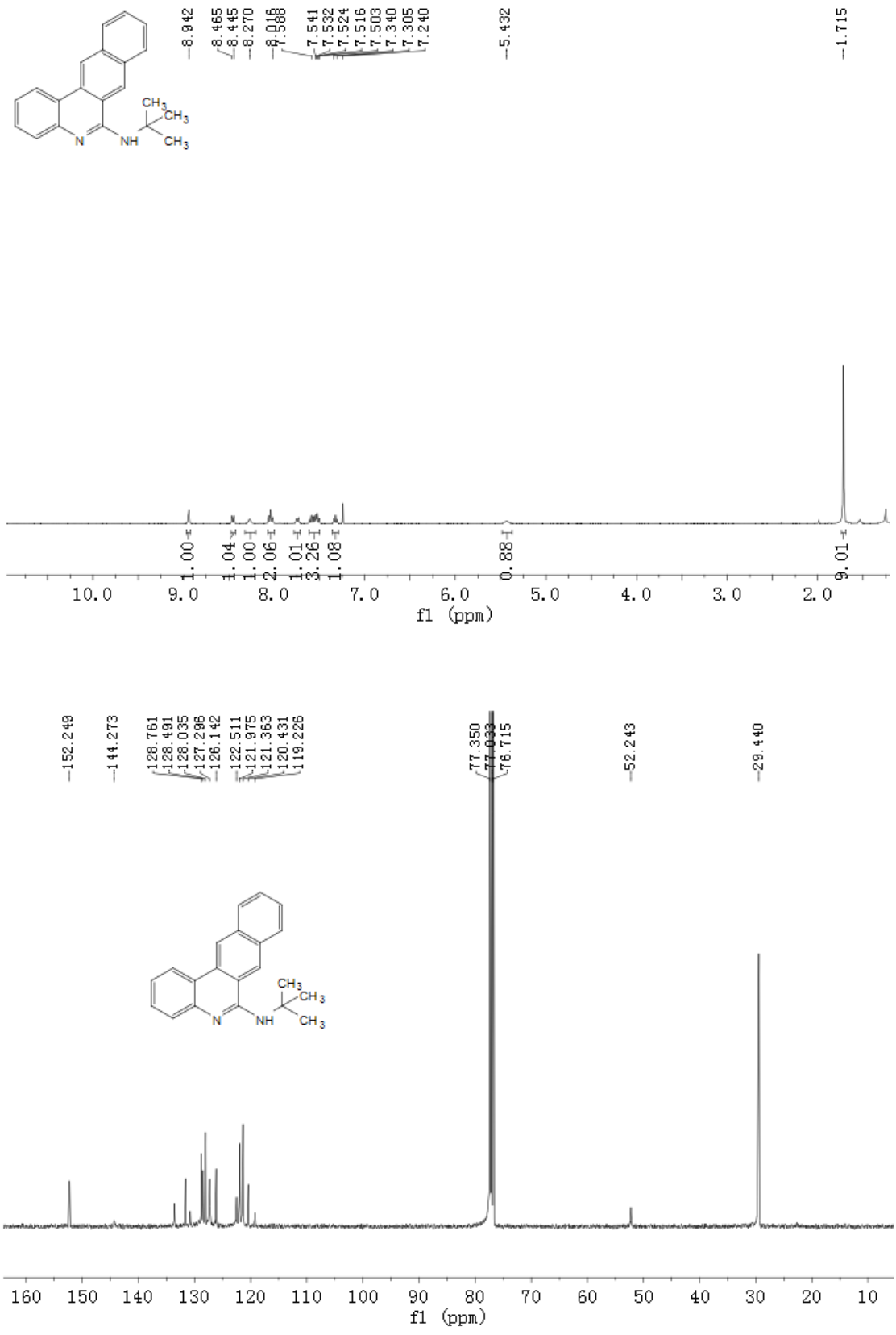
methyl *N*-(tert-butyl)-9-isopropylphenanthridin-6-amine (3ja)

N-(tert-butyl)-9-chlorophenanthridin-6-amine (3ka)

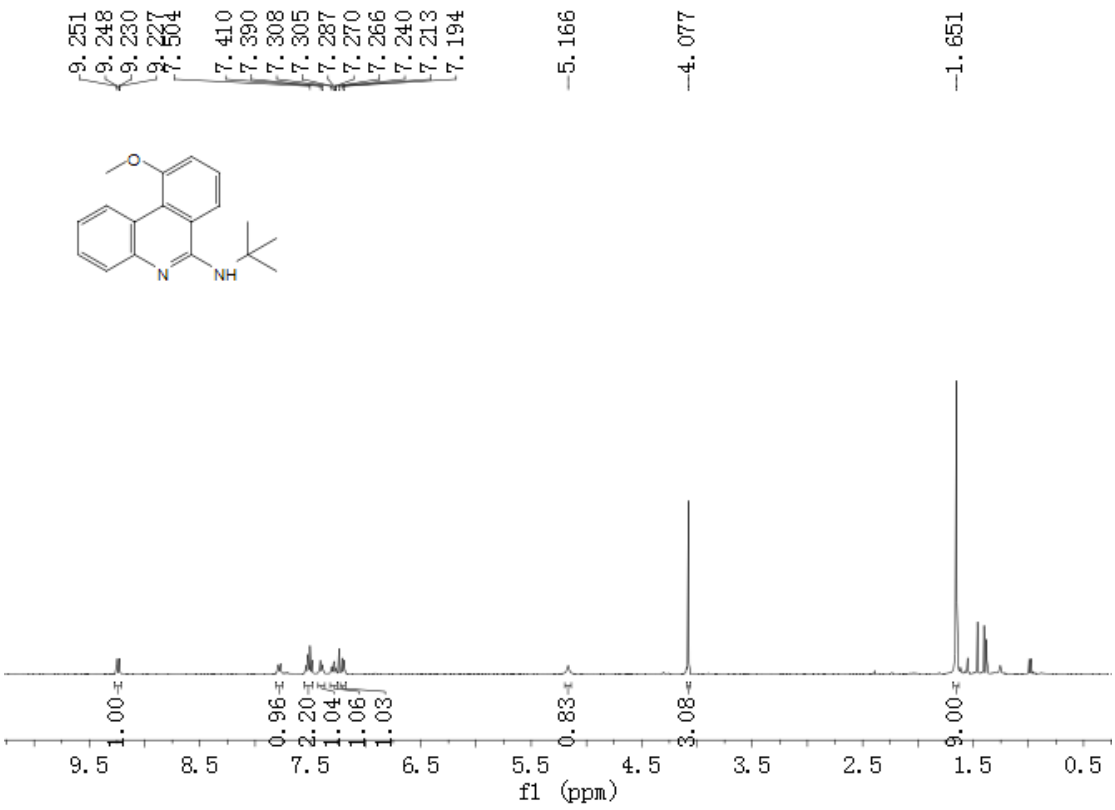


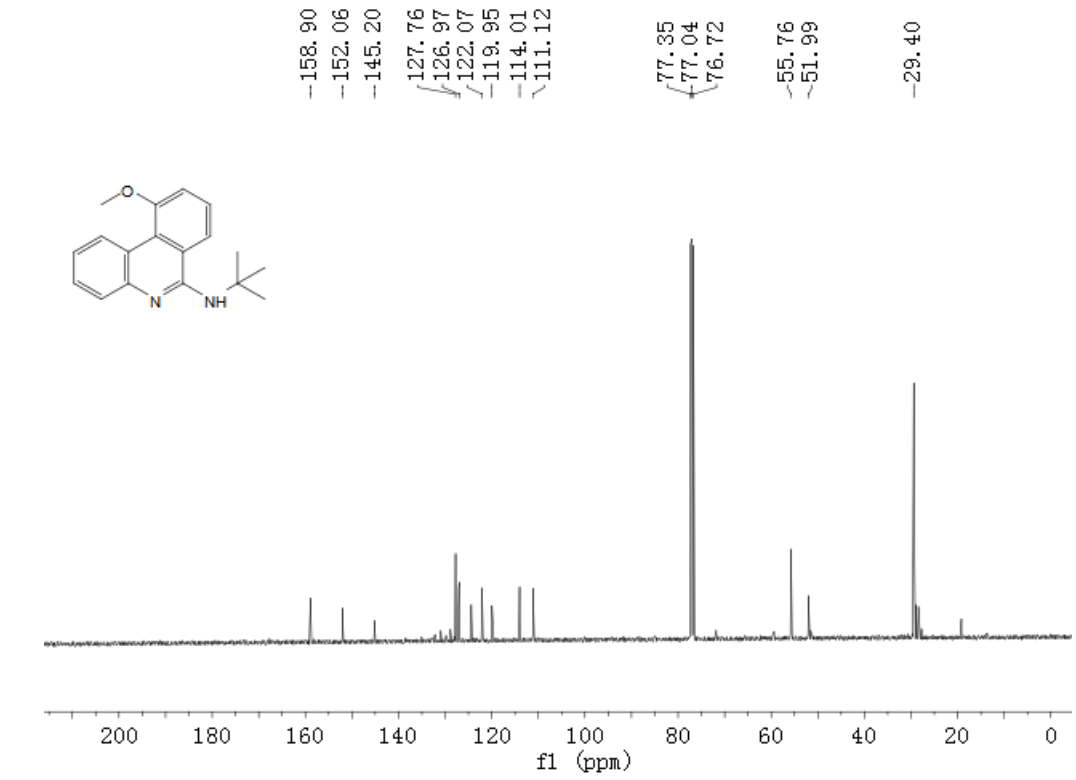


N-(tert-butyl)benzo[j]phenanthridin-6-amine (3la)

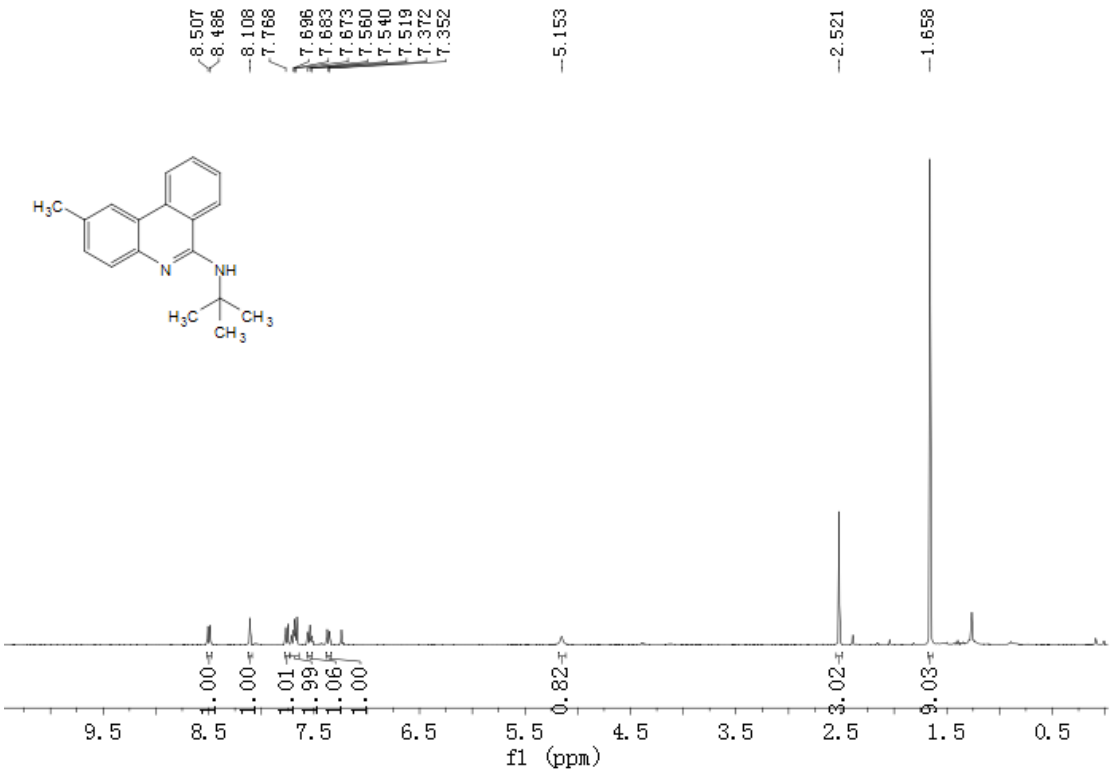


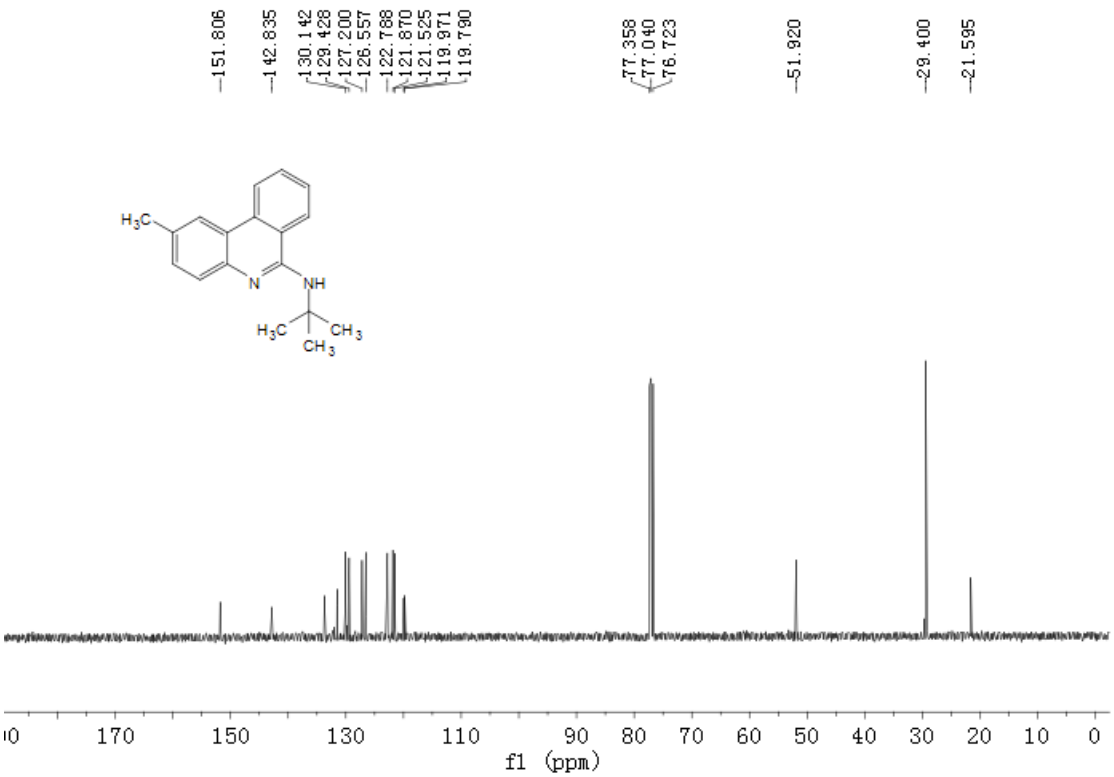
N-(tert-butyl)-10-methoxyphenanthridin-6-amine (3ma)



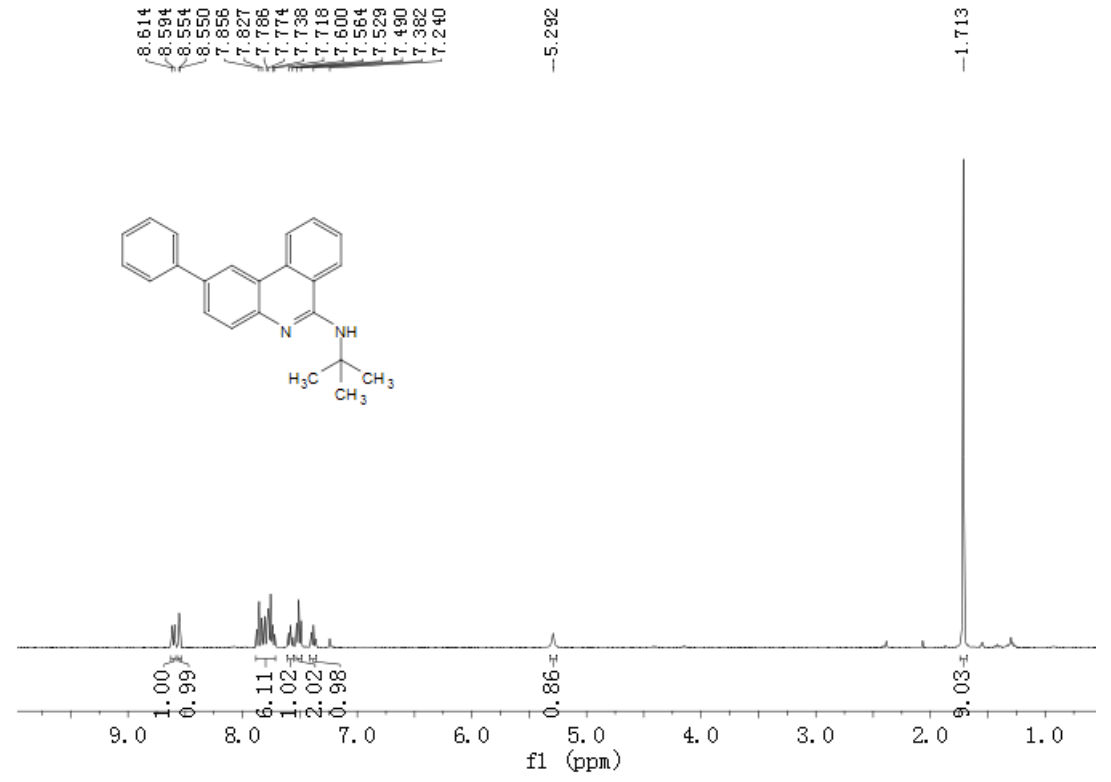


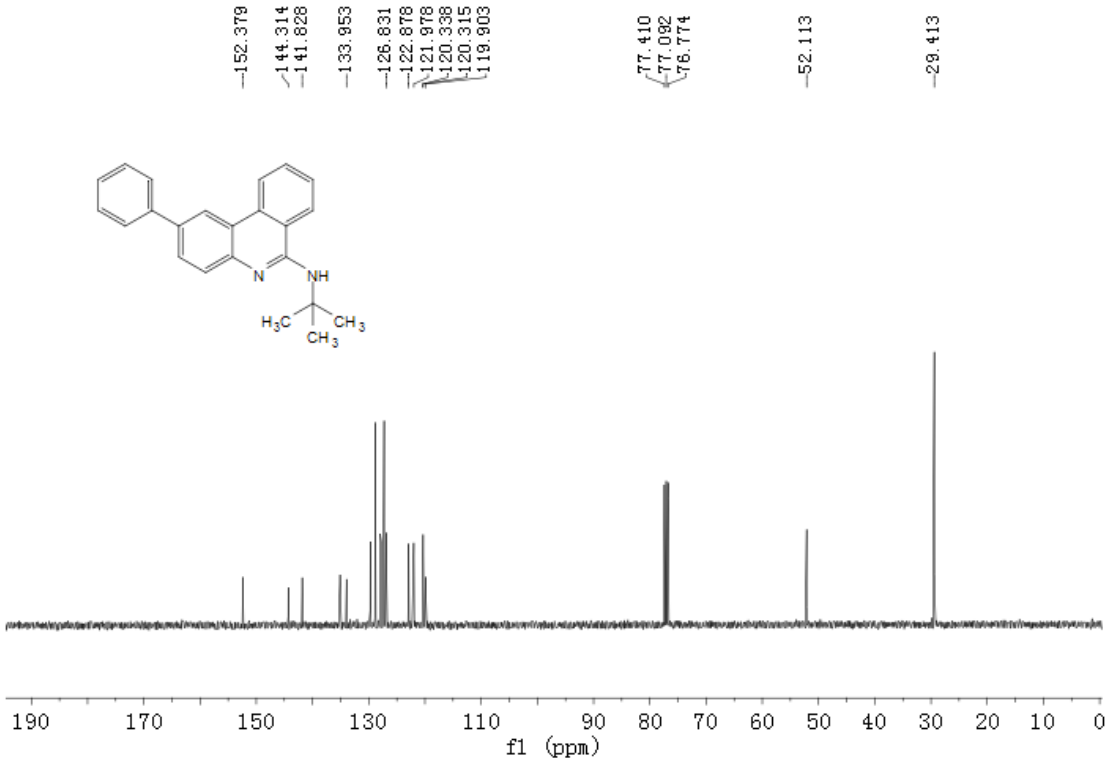
N-(tert-butyl)-2-methylphenanthridin-6-amine（3na）



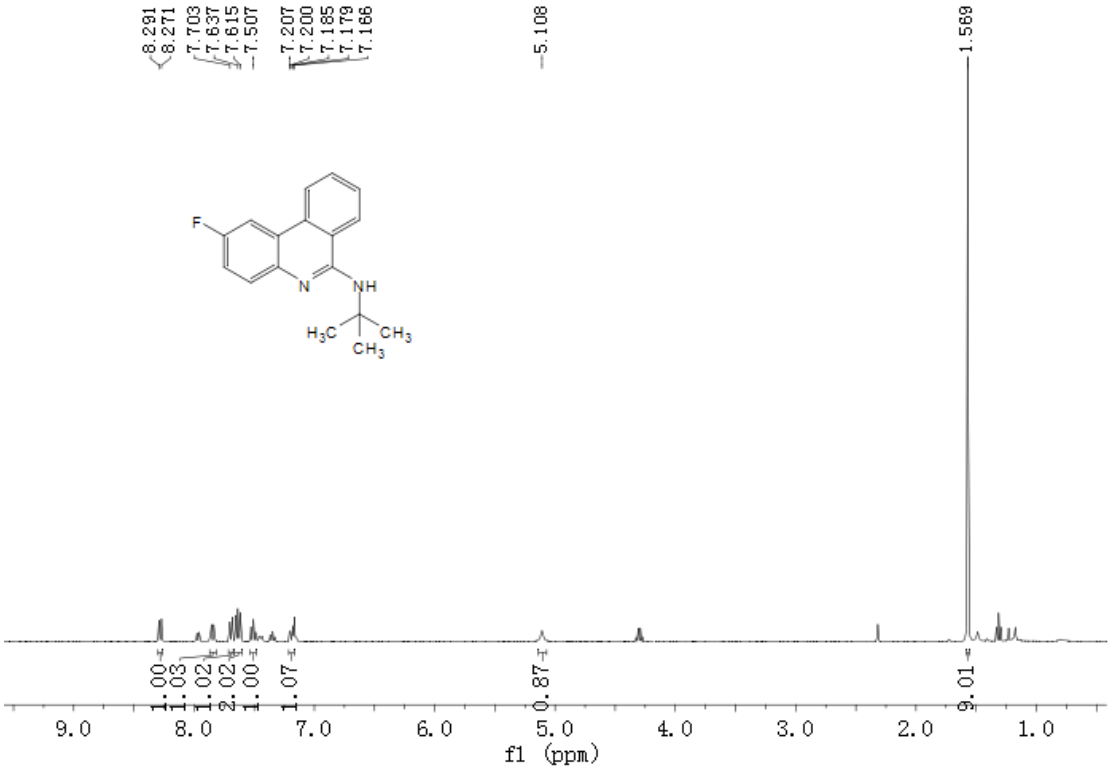


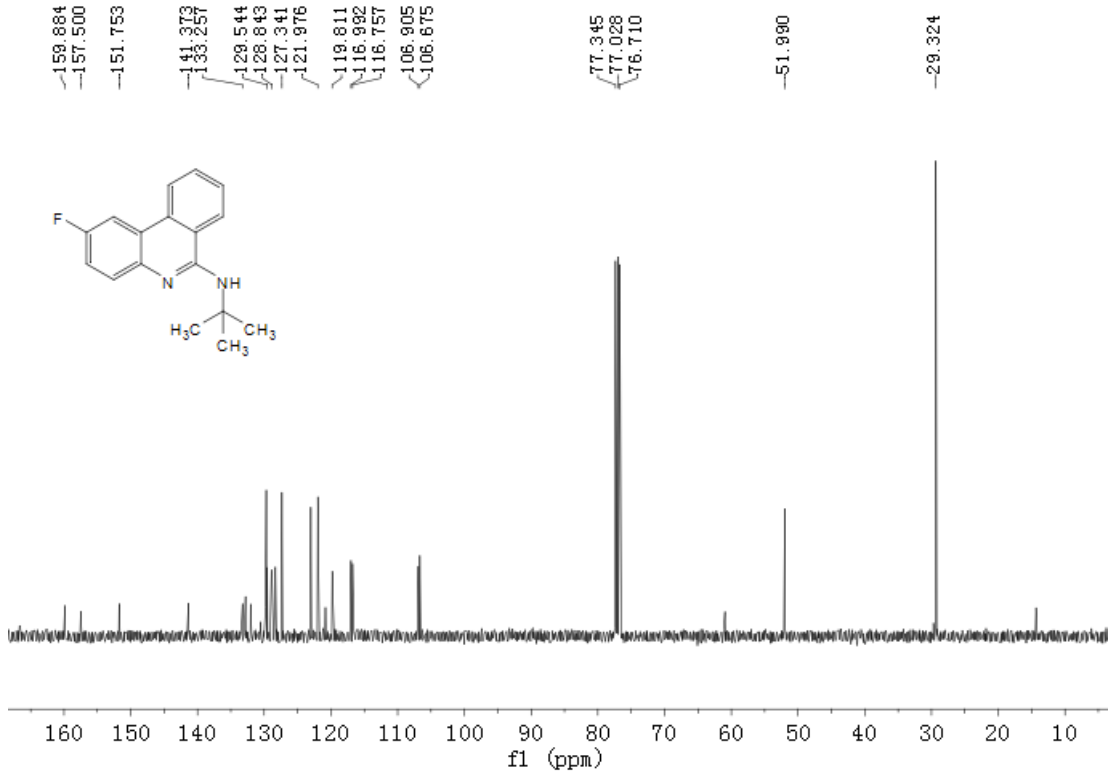
N-(tert-butyl)-2-phenylphenanthridin-6-amine（3oa）



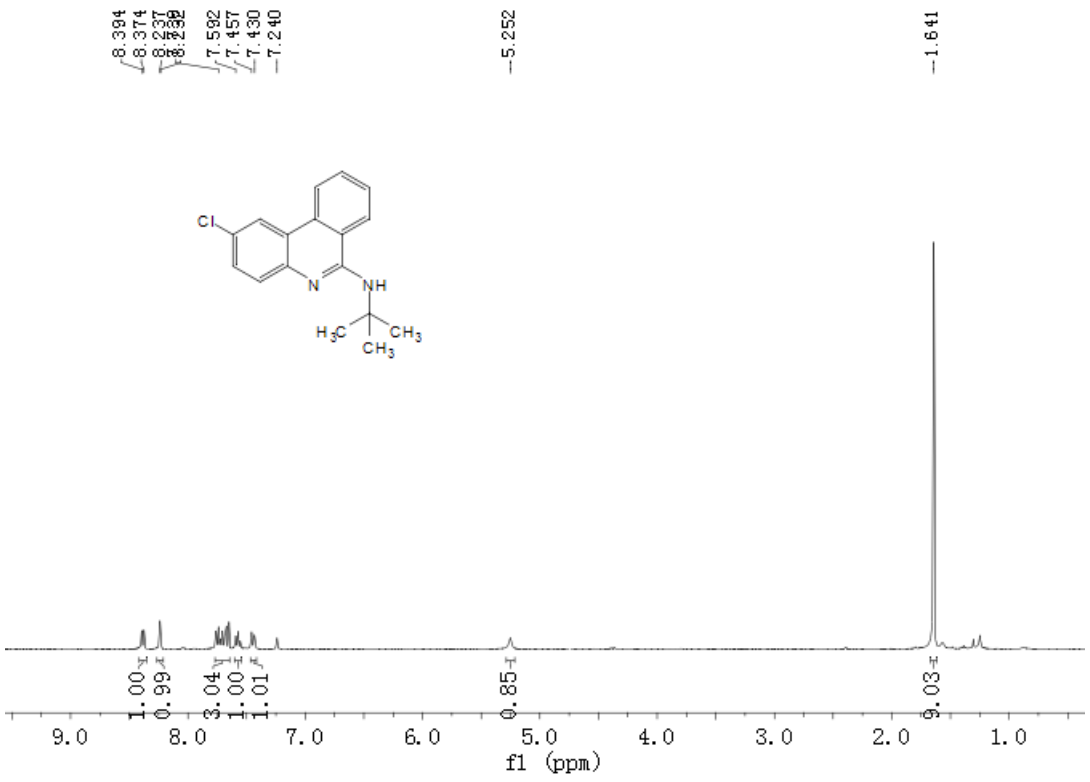


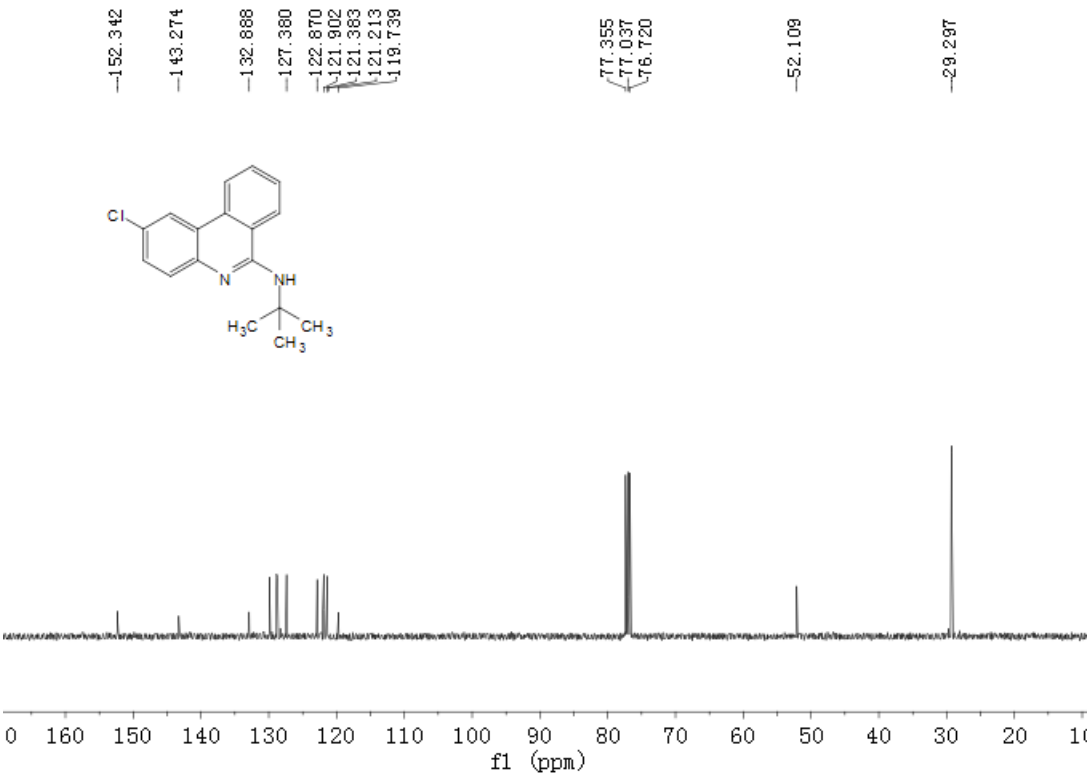
N-(tert-butyl)-2-fluorophenanthridin-6-amine (3pa)



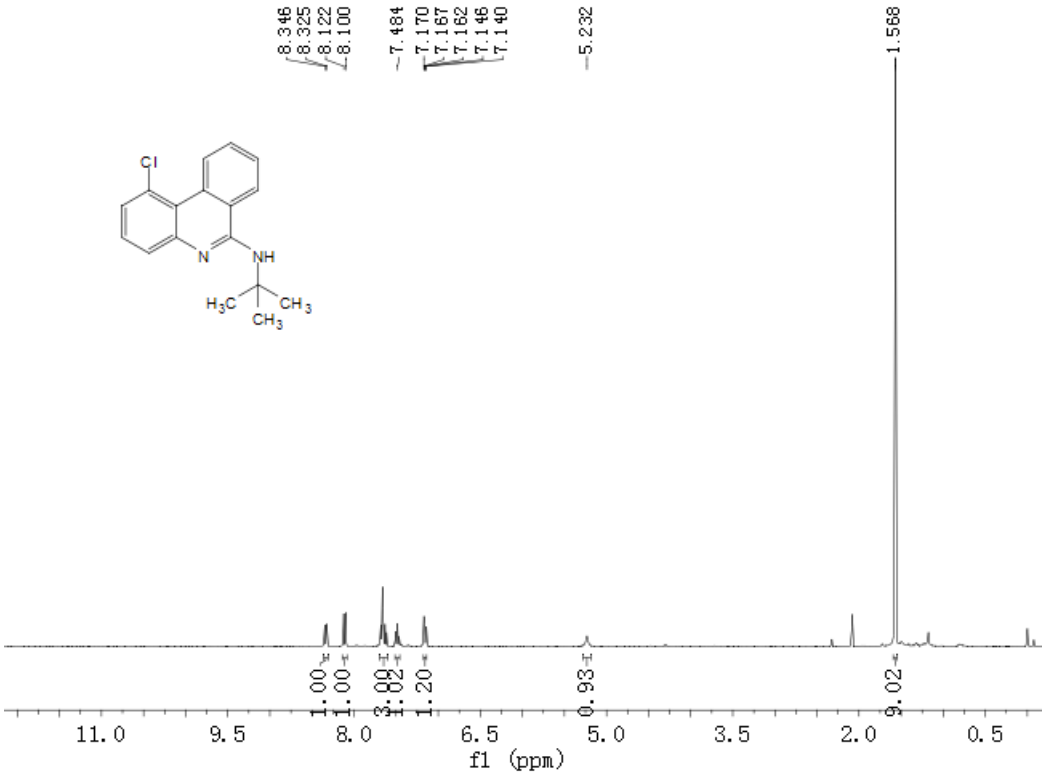


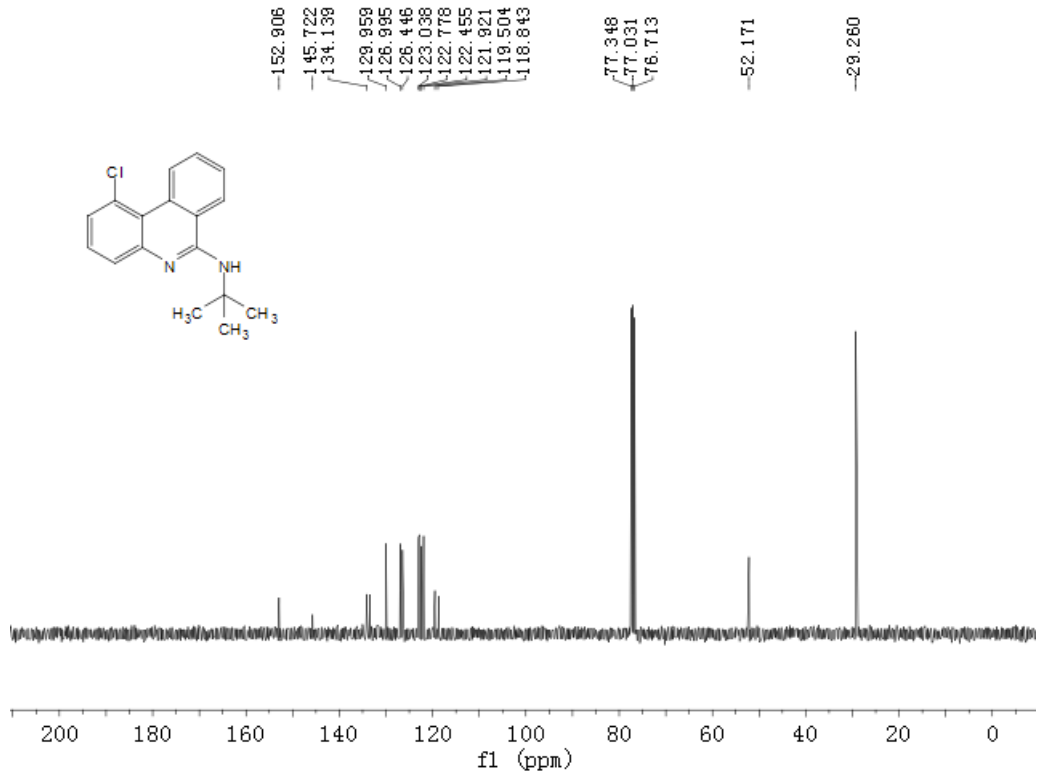
N-(tert-butyl)-2-chlorophenanthridin-6-amine (3qa)



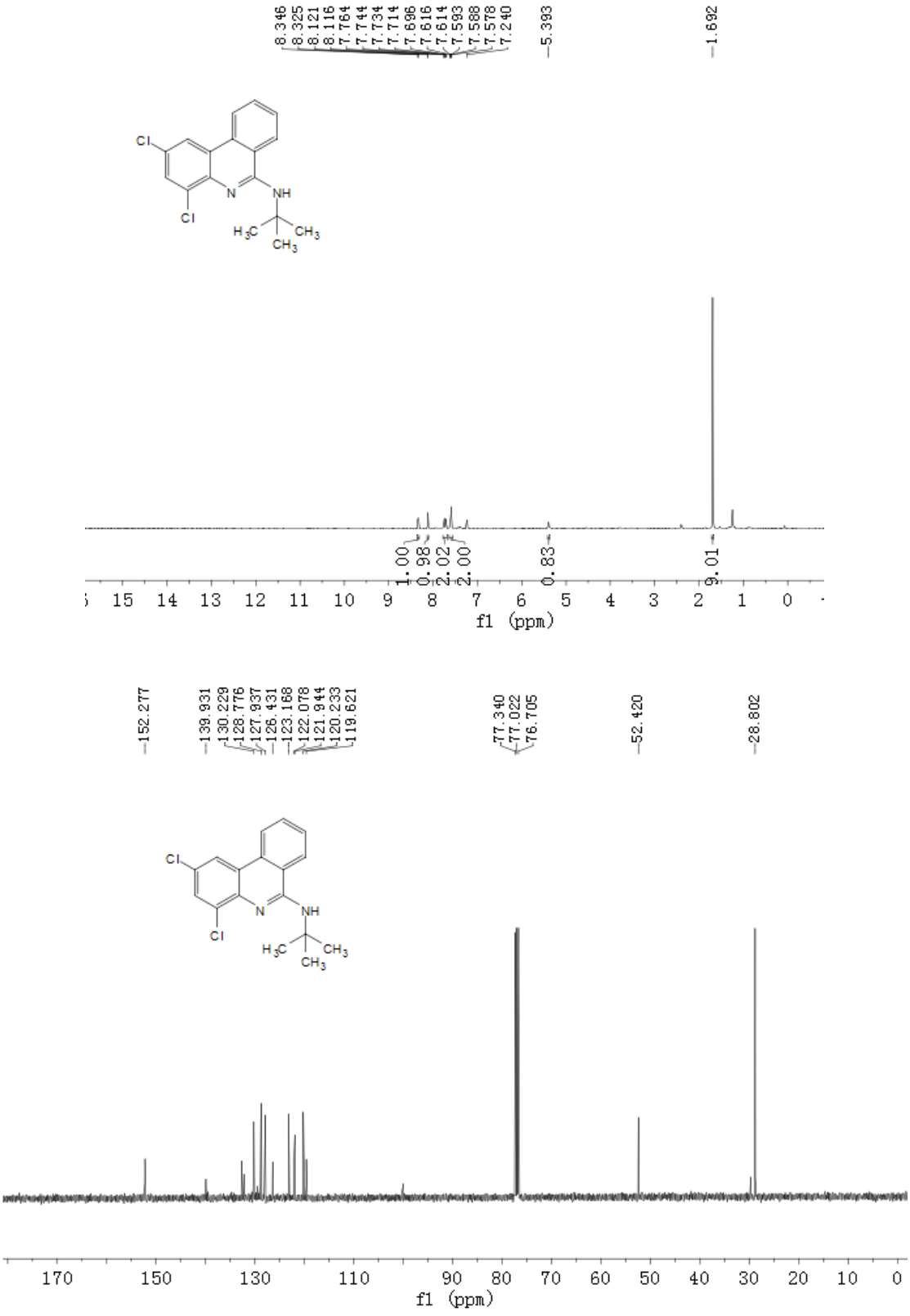


N-(tert-butyl)-1-chlorophenanthridin-6-amine (3ra)

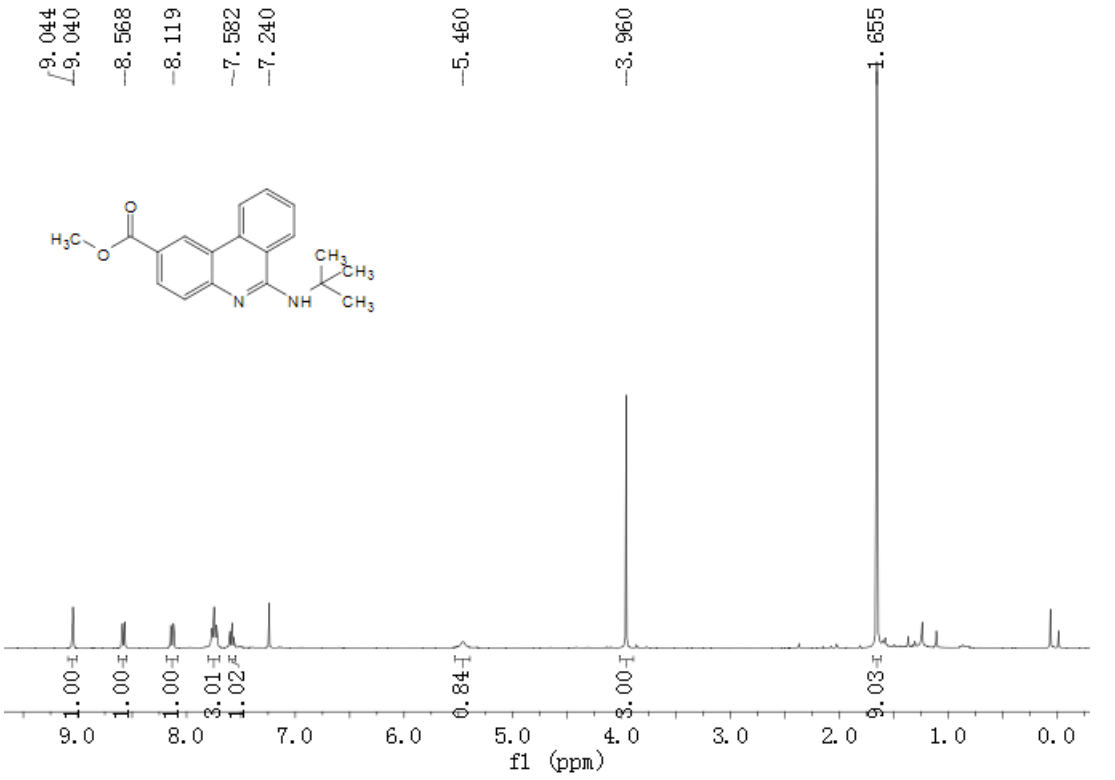


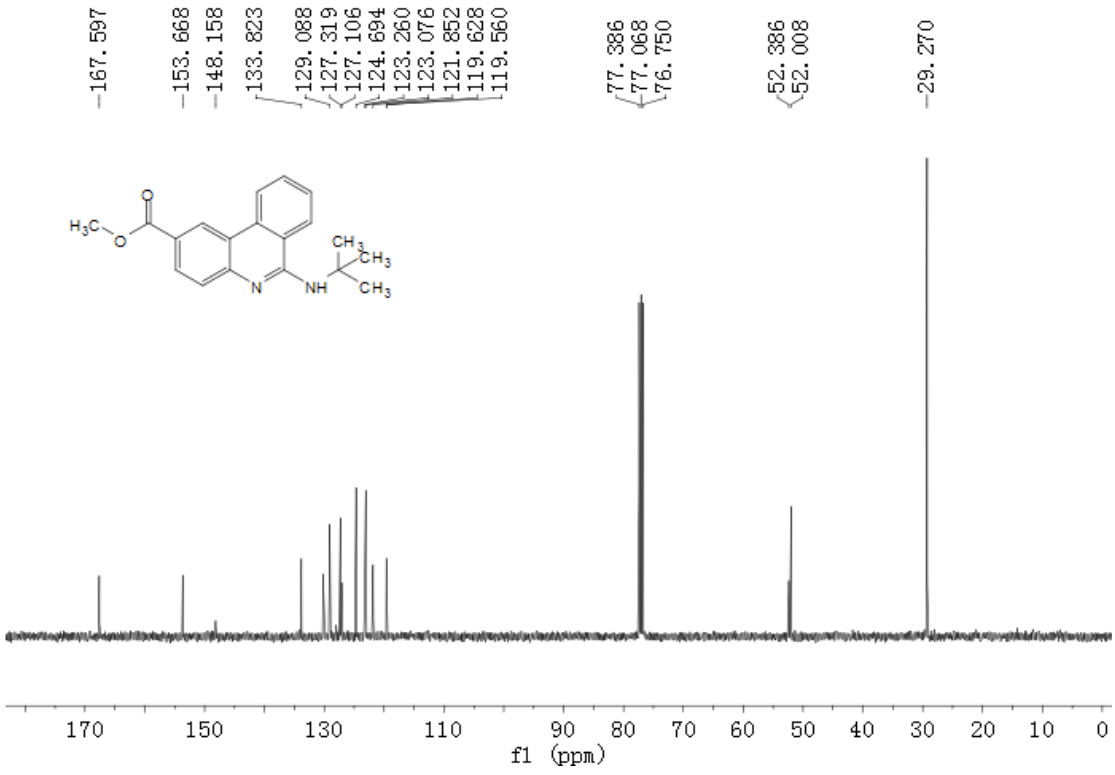


N-(tert-butyl)-2,4-dichlorophenanthridin-6-amine (3sa)

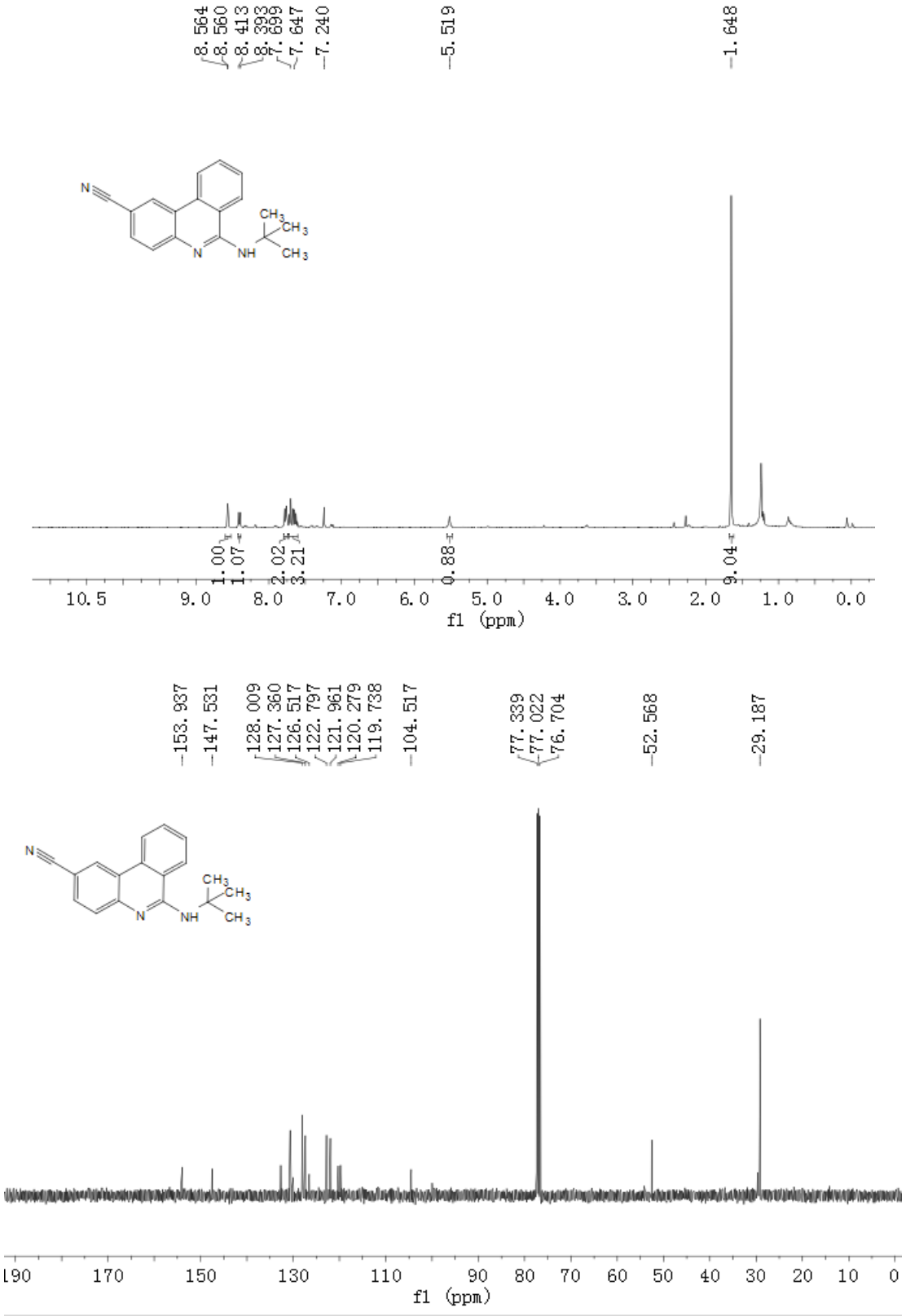


methyl 6-(tert-butylamino)phenanthridine-2-carboxylate (3sa)

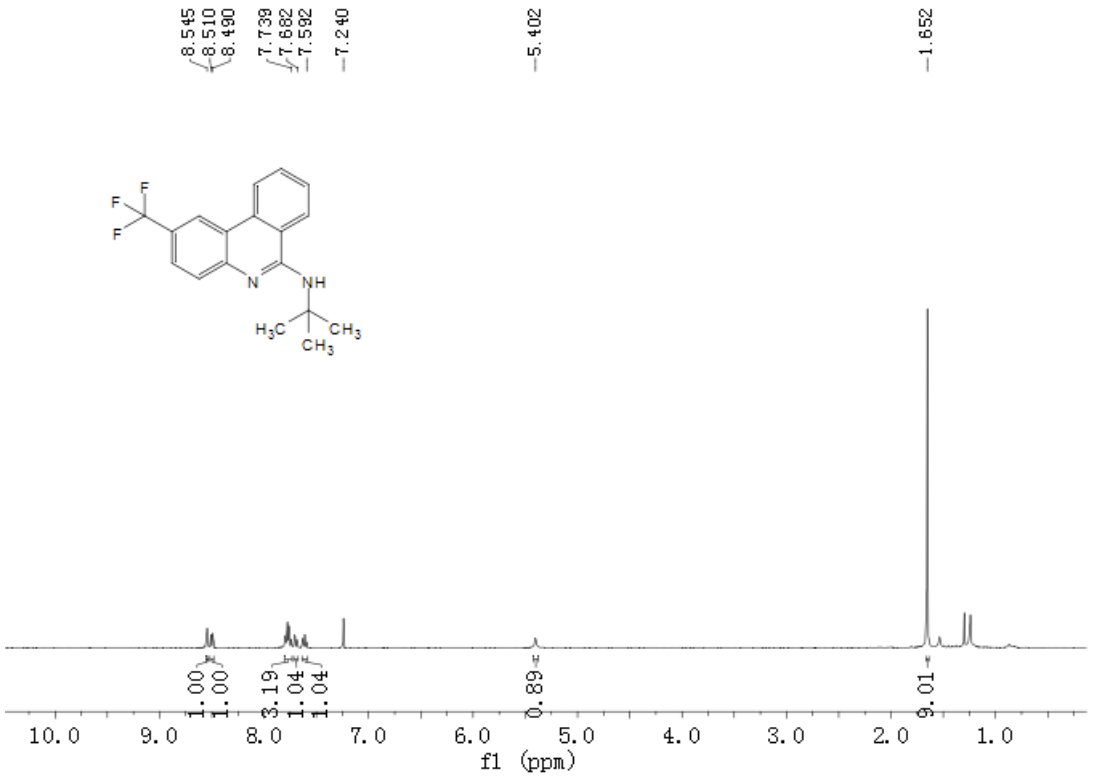


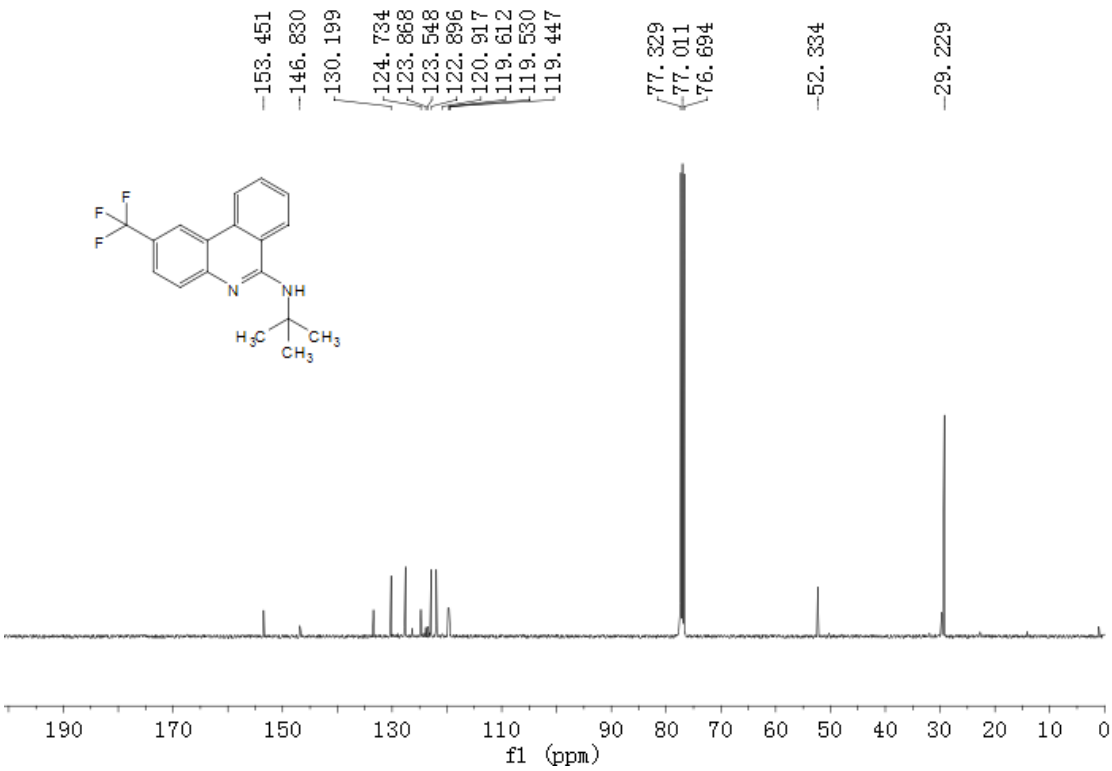


6-(tert-butylamino)phenanthridine-2-carbonitrile (3ua)

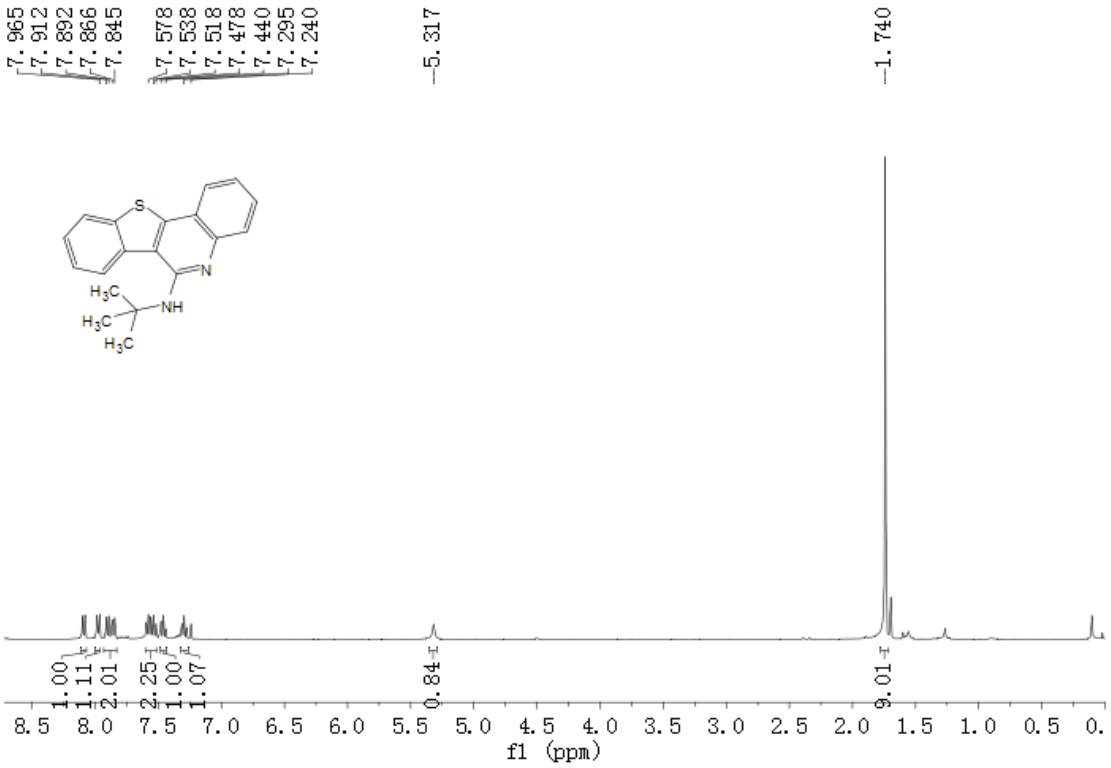


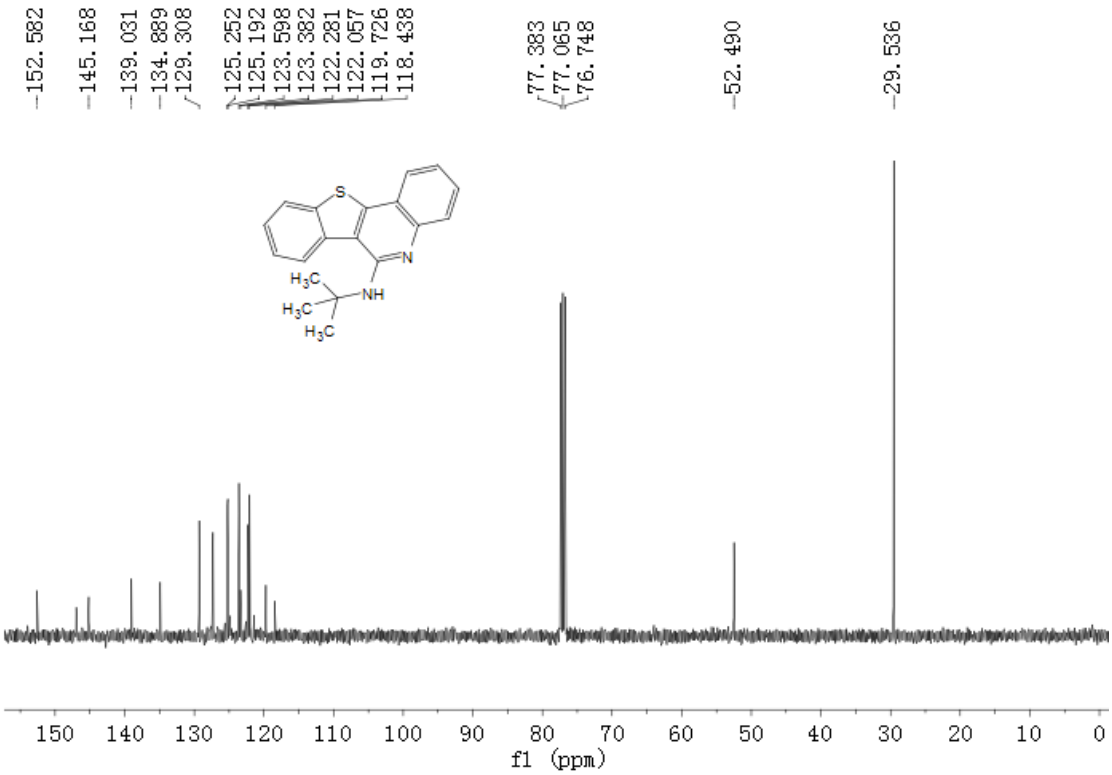
N-(tert-butyl)-2-(trifluoromethyl)phenanthridin-6-amine (3va)



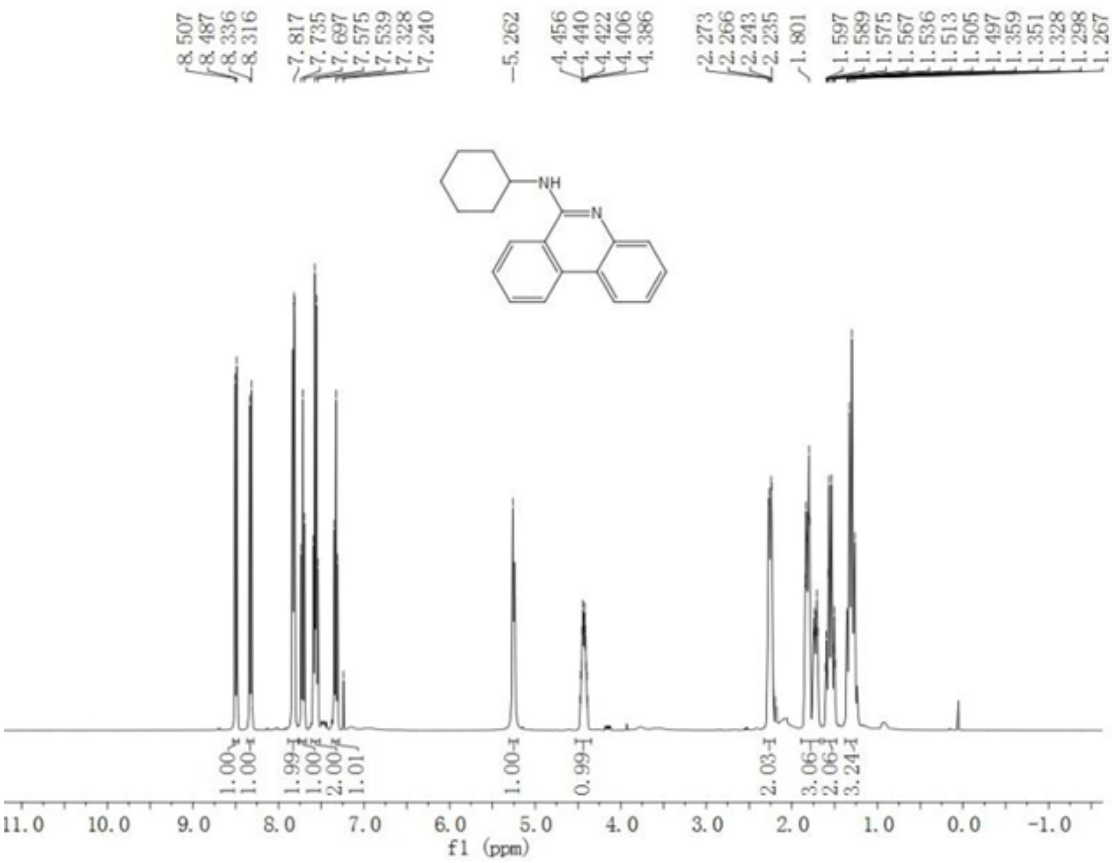


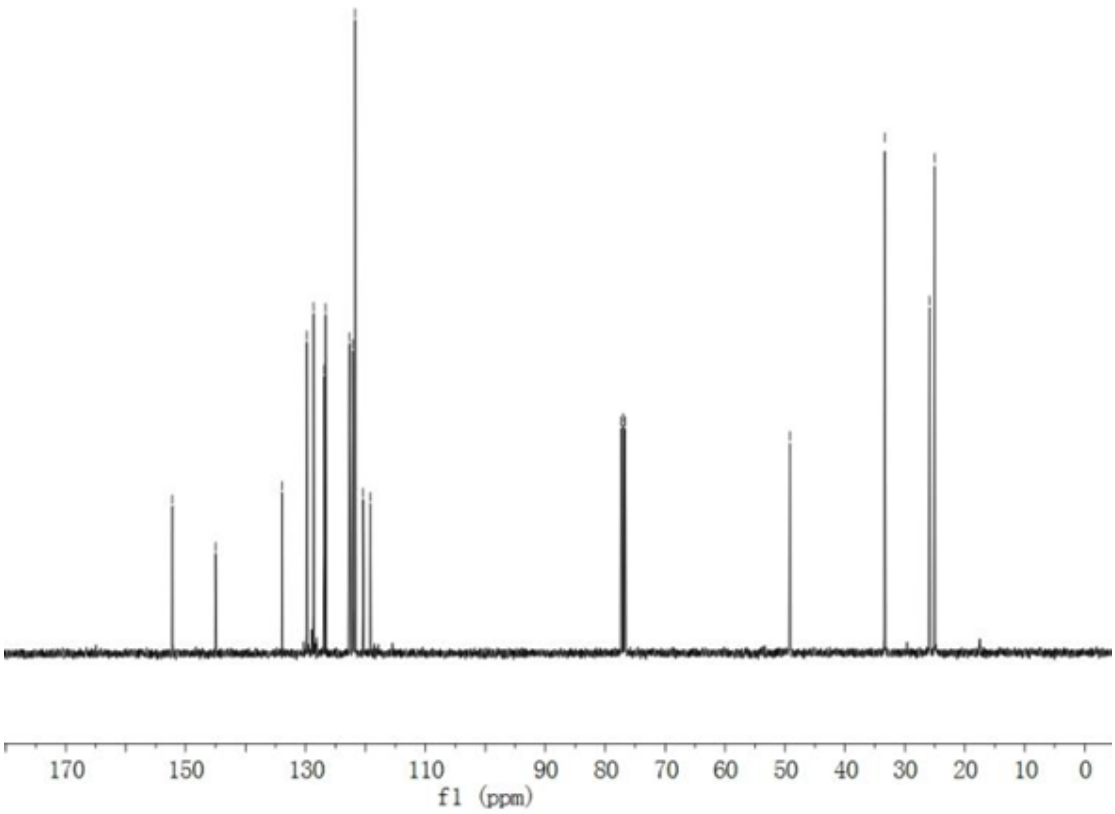
N-(*tert*-butyl)benzo[4,5]thieno[3,2-c]quinolin-6-amine (3wa)



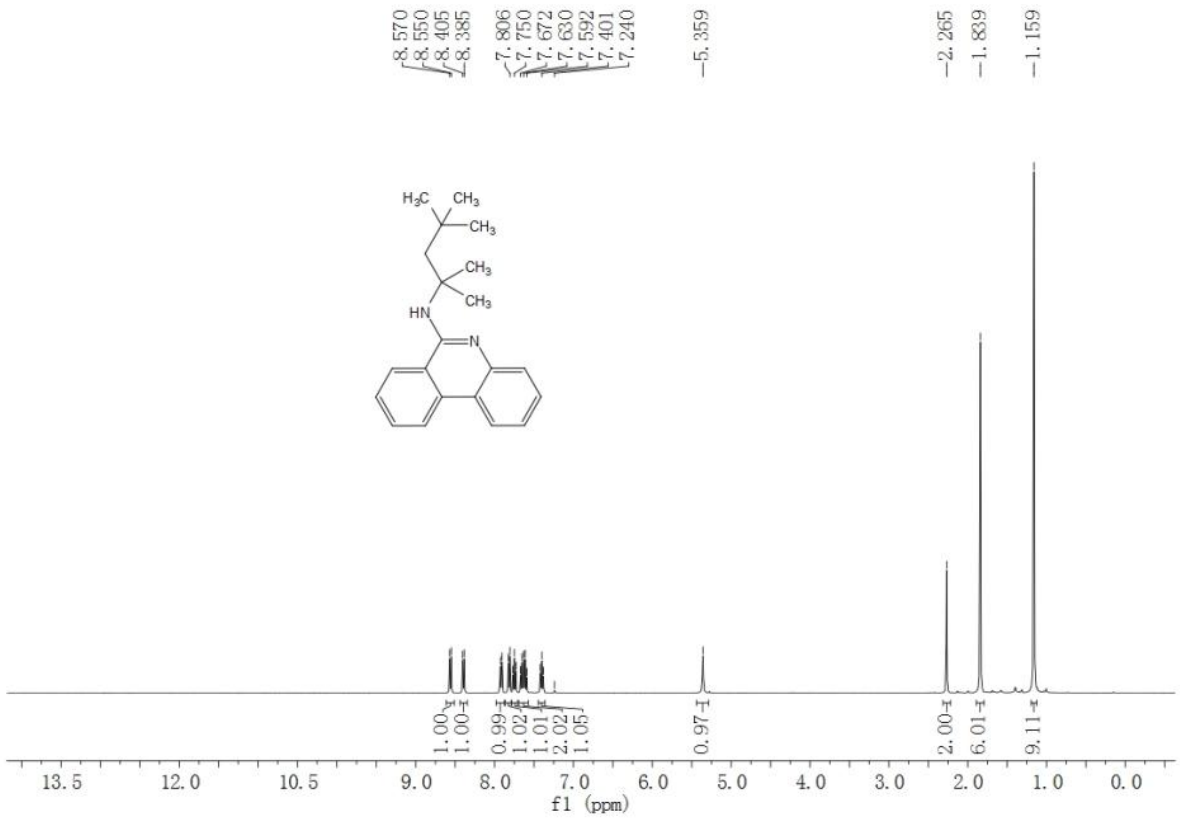


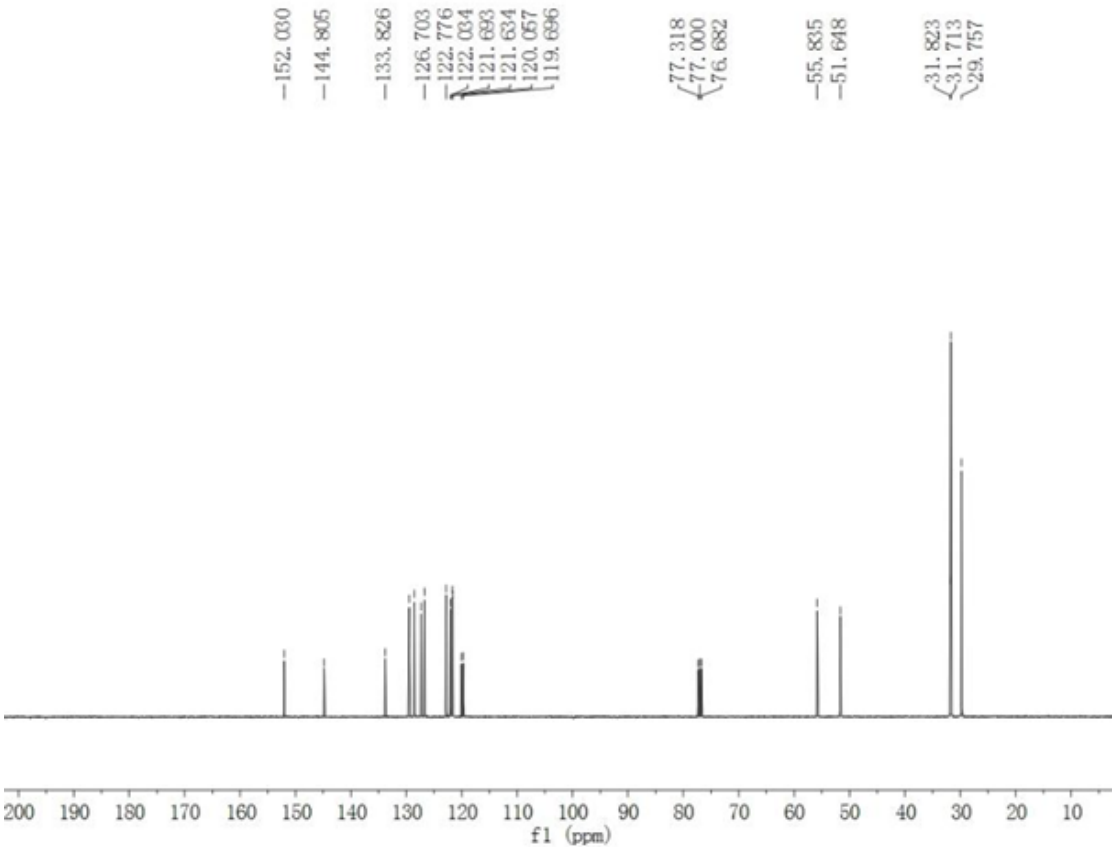
***N*-cyclohexylphenanthridin-6-amine(3ab)**



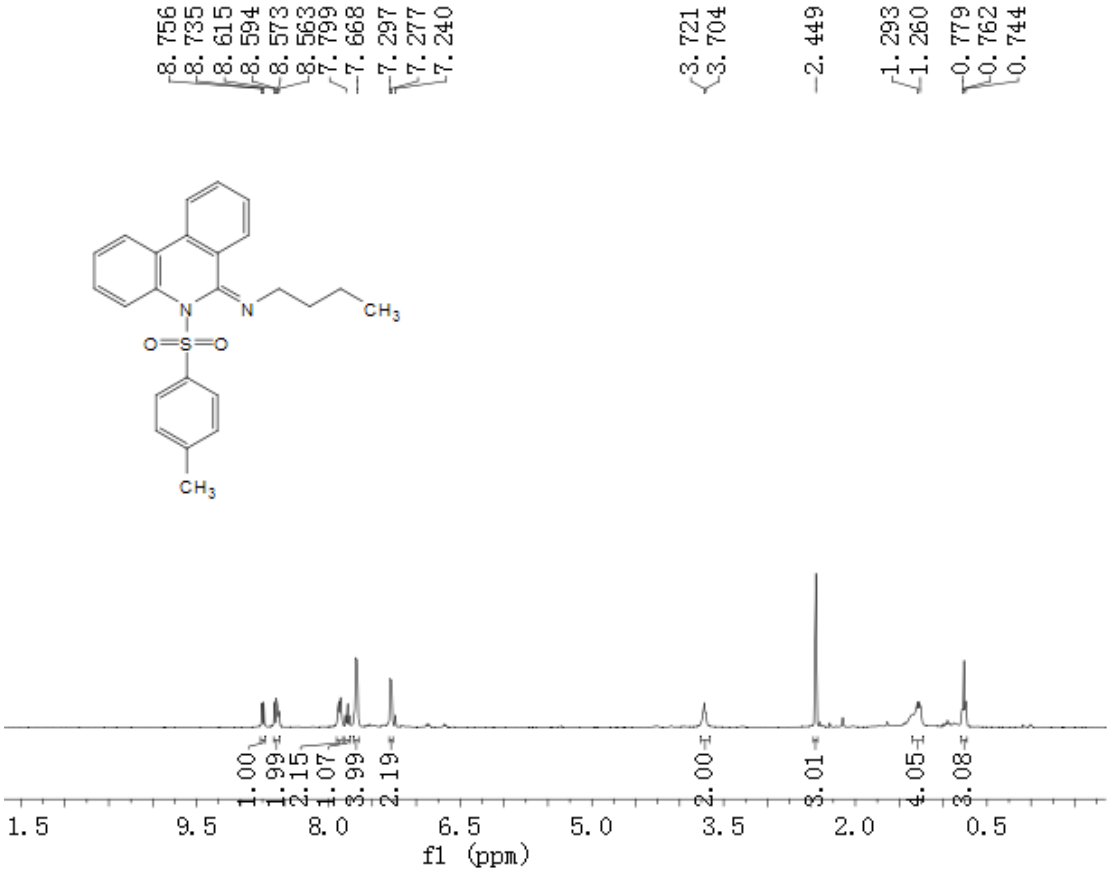


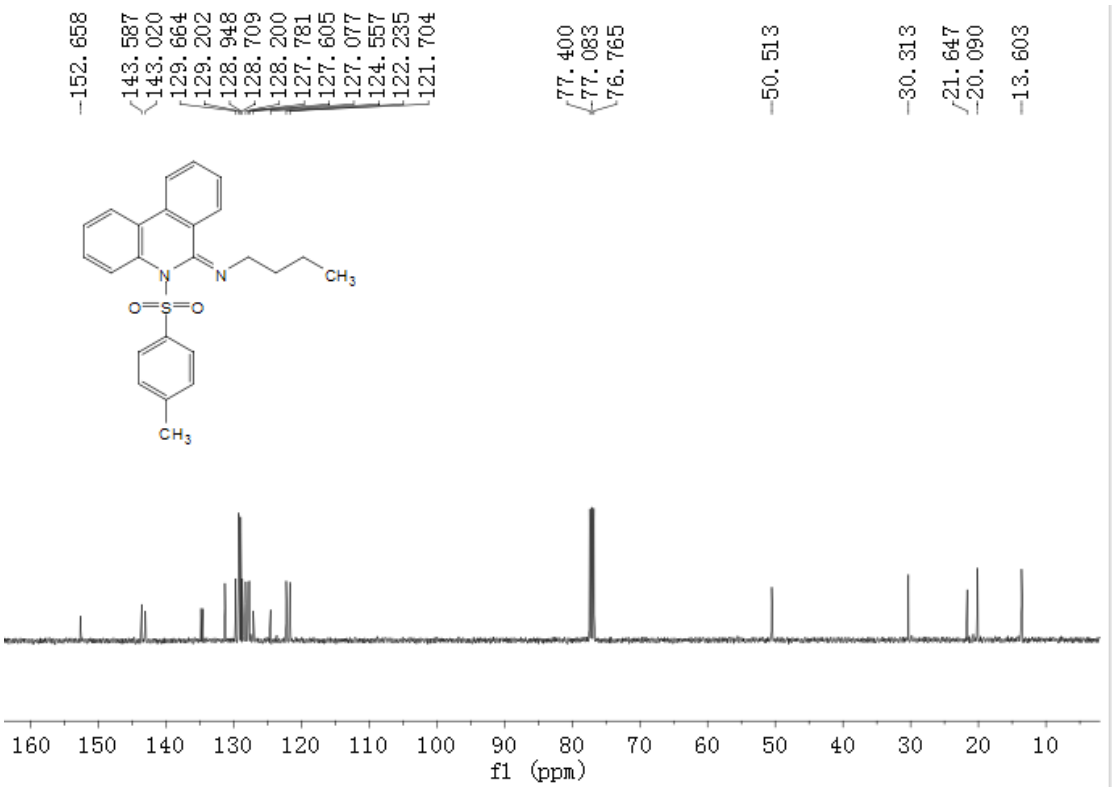
***N*-(2,4,4-trimethylpentan-2-yl)phenanthridin-6-amine (3ac)**


8.570
8.550
8.405
8.385
7.806
7.750
7.672
7.630
7.592
7.401
7.240
5.359
2.265
1.839
1.159
H3C
CH3
CH3
CH3
CH3
HN
N
1.00
1.00
0.99
1.02
1.01
2.02
1.05
0.97
2.00
6.01
9.11
13.5
12.0
10.5
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
f1 (ppm)

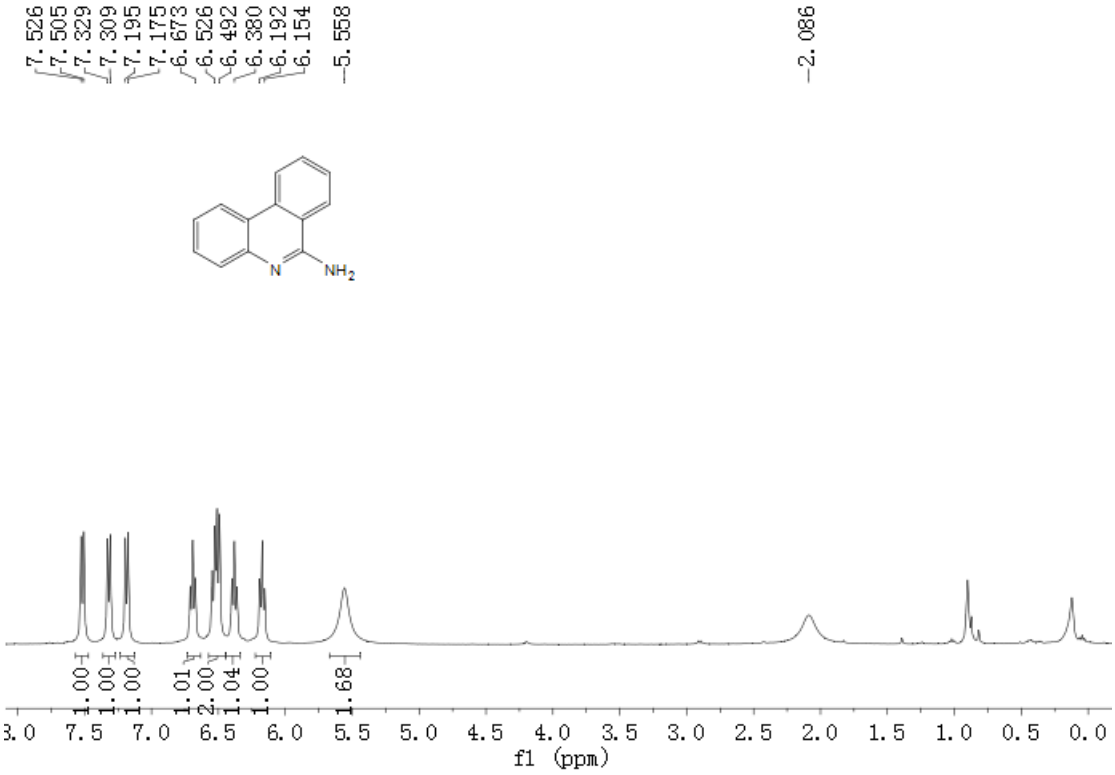

152.030
144.805
133.826
126.703
122.776
122.034
121.693
121.634
120.057
119.696
77.318
77.000
76.682
55.835
51.648
31.823
31.713
29.757
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

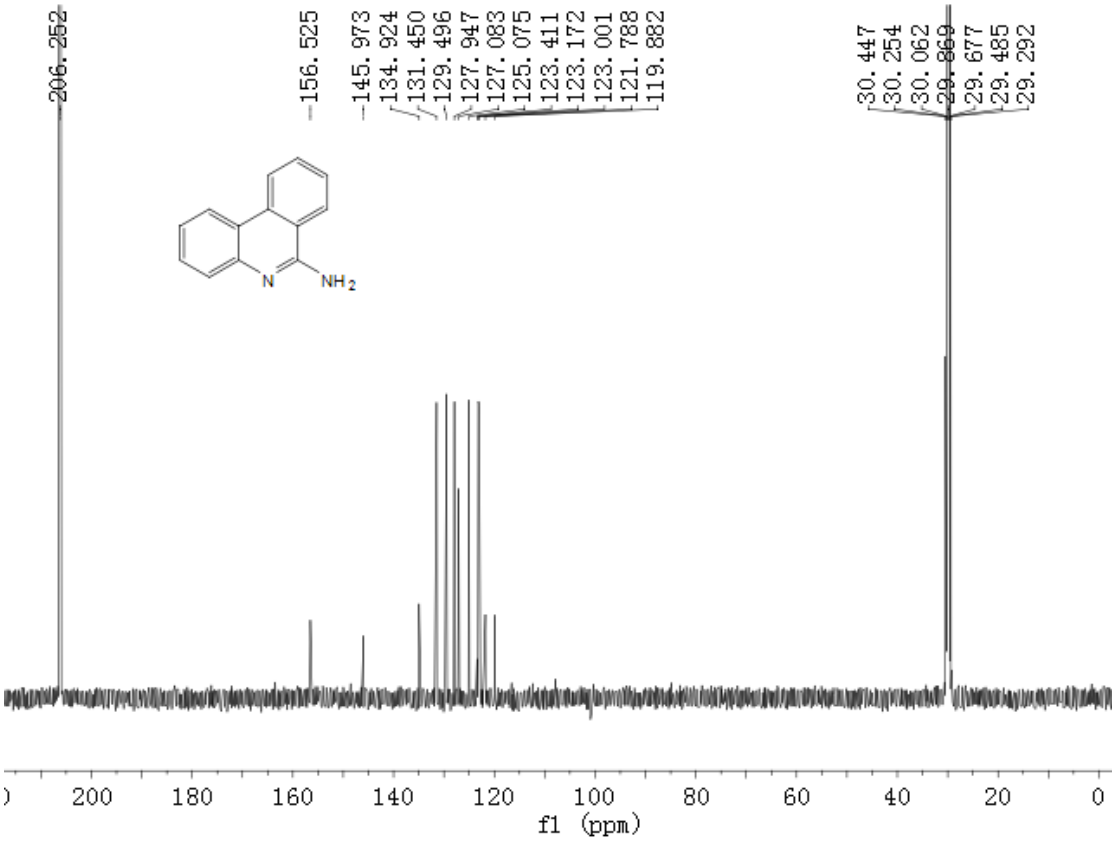
(E)-2-methyl-*N*-(5-tosylphenanthridin-6(5H)-ylidene)propan-2-amine



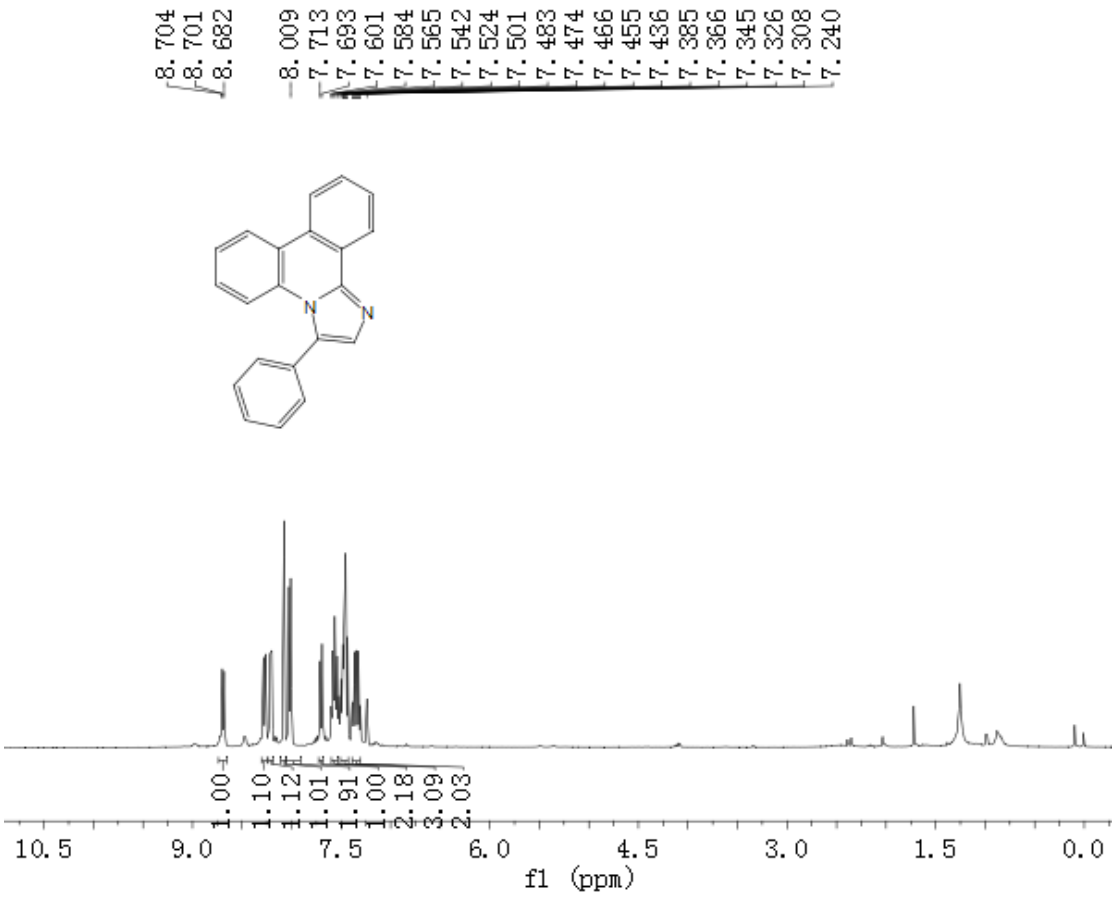


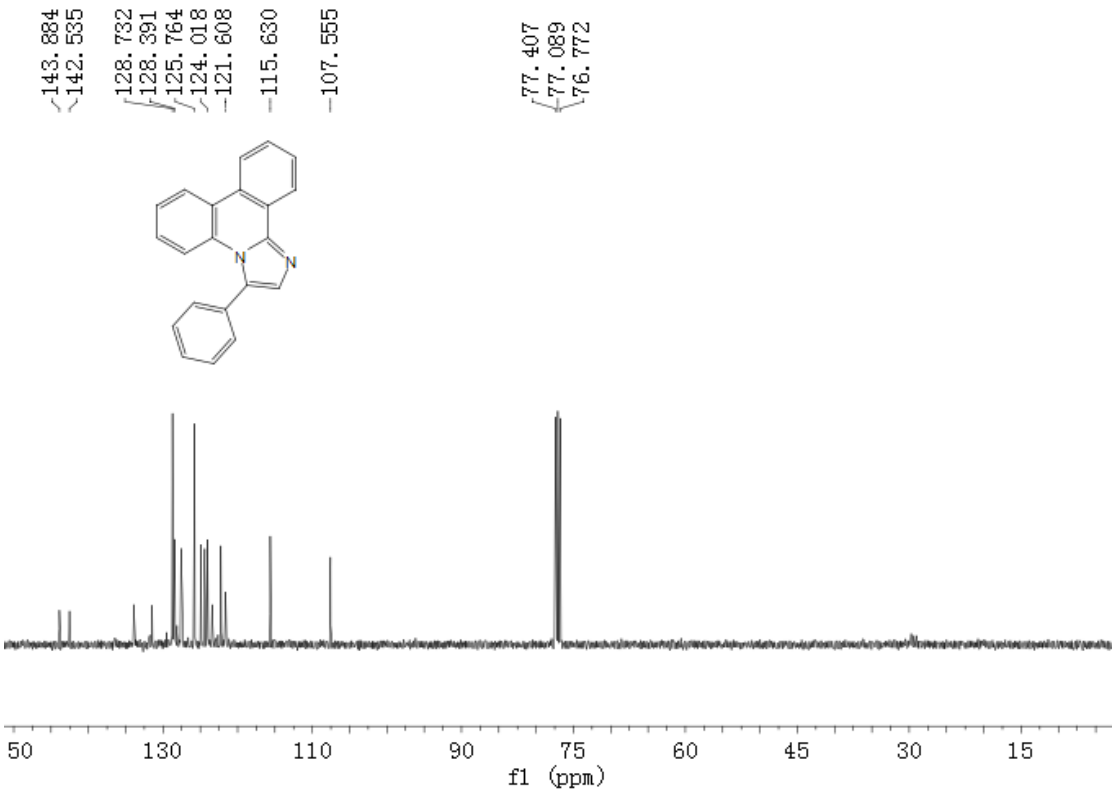
phenanthridin-6-amine (4)





3-phenylimidazo[1,2-f]phenanthridine (5)





NOE Spectra for Compound 9-methylphenanthridin-6-amine (3ia)